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Organic and Organotin Compounds Leached from PVC and CPVC Pipe

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ORGANIC AND ORGANOTIN COMPOUNDS LEACHED FROM PVC AND CPVC PIPE

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16. ABSTRACT

The primary objective of this research program was to determine whether organotins, contained in heat stabilizers of polyvinyl chloride (PVC) and chlorinated polyvinyl chloride (CPVC) pipe, and other organics present in pipe sealing cement solvents may leach into potable water supplies. Analytical methods for concentrating, separating identifying, and quantitating these chemicals were evaluated. The hydride generation/atomic absorption methods of Hodge, Braman, and others and a Grignard derivatization technique, followed by gas chromatography mass spectrometry, were used to characterize samples of standard extractant water exposed to PVC and CPVC pipe, both fragmented and loops constructed using pipe cement. Analyses revealed that alkyltin species and organi pipe cement solvents can leach into potable water. The organotin leaching appears to occur in a biphasic manner. The concentration of dimethyltin (as dichloride) in the extract water exposed to a PVC pipe loop at 37°C was 45 ppb on Day 1 and decreased from 3.0-0.25 ppb/24 hrs from Days 2-22. The concentration of butyltin (as dichloride) in the extractant water exposed to a CPVC pipe loop at 72°C was 2.6 ppb on Day 1 and decreased from 1.0 to 0.03 ppb/24 hrs during the ensuing 21 days. Methyl ethyl ketone, tetrahydrofuran and cyclohexanone leached into the water in a miniature pipe loop for more than 14 days. The concentrations of these solvents ranged from 10 ppm to 10 ppb. This data and analytical technology will enable the development of a better understanding of the health hazards associated with the transport of potable water in PVC and CPVC pipes.

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FOREWORD

The U.S. Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimony to the deterioration of our national environment. The complexity of that environment and the interplay between its components require a concentrated and integrated attack on the problem.

Research and devlopment is that necessary first step in problem solution and it involves defining the problem, measuring its impact, and searching for solutions. The primary mission of the Health Effects Research Laboratory in Cincinnati (HERL) is to provide a sound health effects data base in support of the regulatory activities of the EPA. To this end, HERL conducts a research program to identify, characterize, and quantitate harmful effects of pollutants that may result from exposure to chemical, physical, or biological agents found in the environment. In addition to the valuable health information generated by these activities, new research techniques and methods are being developed that contribute to better understanding of human biochemical and physiological functions, and how these functions are altered by low-level insults.

This report describes the development and application of analytical techniques for determining organotins and other organics in aqueous solutions, particularly standard extract of polyvinyl chloride (PVC) and chlorinated polyvinyl chloride (CPVC) pipe systems. The extraction of ppb levels of methyl and butyl tins (as dichlorides) and ppb to ppm levels of methyl ethyl ketone, tetrahydrofuran, and cyclohexane (volatile organic solvents used in PVC and/or CPVC pipe cements) is reported. With this data and the analytical ability for additional measurements of these chemicals, we may develop a better understanding of the health hazards that may be associated with the transport of potable water in PVC and CPVC pipe.

James B. Lucas, M.D.
Acting Director
Health Effects Research Laboratory

ABSTRACT

The primary objective of this research program was to determine whether or not organic forms of tin existed in potable water samples after contact with either polyvinyl chloride (PVC) or chlorinated polyvinyl chloride (CPVC) pipe containing organotin heat stabilizers. Analytical techniques to identify and quantitate organotin compounds at concentrations below one part per billion (ppb) were explored and refined. Four test protocols were used to simulate the extraction process. First, during method development, fragmented pipe samples were digested with extractant water in order to obtain high surface-to-volume ratios, resulting in higher organotin concentrations than would be encountered in the field. Second, extractant water was continuously pumped through an 8.9-meter rectangular closed loop of one-inch internal diameter pipe having an inner surface area of 0.71 m^2 (1100 in^2), maintained at constant temperature. This system was used to provide sequential samples over a 22-day period, during which time the extractant water was completely removed for analysis and replaced at two- to four-day intervals. Third, a miniature pipe system attached to a laboratory faucet was used primarily to study the fate of the solvents incorporated in cements used to join segments of pipe. Fourth, incubation of short lengths of pipe with extractant water served as a convenient method to study changes in leach rates as experimental parameters such as pH were varied.

Commercial pipe samples stabilized with dialkyltin-bis-isooctylthioglycolate compounds were tested. The extractant water was synthesized from doubly-distilled water with 100 mg/L hardness (as calcium carbonate), 84 mg/L buffer (sodium bicarbonate), and 1.0 mg/L chlorine. A pH of 5.0 ± 0.2 was obtained by bubbling with carbon dioxide. This is similar to the "Standard" Extractant Water used by the National Sanitation Foundation.

Organotin analysis at these very low levels utilized hydride derivatization, followed by collection of the hydrides on glass bead or OV-1 traps immersed in liquid nitrogen, and detection of tin by atomic absorption spectrophotometry as each hydride eluted sequentially from the trap after the liquid nitrogen was removed. The exact organotin species from which these hydrides arose were not identified, although there was evidence that they existed in ionic form in the extractant water. No evidence of the sulfur-containing part of the stabilizer was found in the extractant water.

The results showed that alkyltin species were extracted from the tested PVC and CPVC pipes by water. The amount of dimethyltin (as the dichloride) leached from PVC into pH 5 extractant water at 37°C was 35 ppb for day one, and decreased from approximately 3.0 to 0.25 ppb per 24 hours, in a biphasic manner, from days 2 through 22. The amount of dibutyltin (as the dichloride) leached from CPVC into pH 5 extractant water at 72°C was 2.6 ppb for day one,

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TYPING GUIDE SHEET

and decreased from 1.0 to 0.03 ppb per 24 hours, again in a biphasic manner, from days 2 through 21.

Volatile organic solvents (methyl ethyl ketone, tetrahydrofuran, and cyclohexanone were monitored) used in the sealing cements applied to PVC and CPVC pipe joints continued to leach into water supplies for more than 14 days using the miniature pipe system. The quantities ranged from 10 ppm to 10 ppb during the 15 days of sampling.

Sufficient toxicological data are not available to assess the health significance of the very low levels of organotin and cement solvent chemicals found in this study. Further analytical work should therefore be done in conjunction with toxicity testing of the extractant water samples.

The University of Michigan has submitted this report in fulfillment of Cooperative Agreement No. CR 806275 sponsored by the U.S. Environmental Protection Agency. This report describes the research performed from November 1, 1978 through December 31, 1980.

CONTENTS

Foreword iii
Abstract iv
Figures ix
Tables xii
Acknowledgments xiii

1. Introduction 1
2. Conclusions and Recommendations 3
3. Materials and Instrumentation 5
    - Pipe and stabilizer samples 5
    - Organotin reference compounds 5
    - Aqueous standards of tin, organotin compounds, and cement solvents 7
    - Preparation of extractant water 8
    - Grignard alkylation and hydride generation reagents 8
    - Atomic absorption 8
    - Gas chromatography 9
    - High-pressure liquid chromatography 9
    - Thin-layer chromatography 9
    - Emission spectroscopy 9
    - Mass spectrometry 9
4. Experimental Procedures 10
    - Hydride generation 11
    - Grignard alkylation 15
    - Quality assurance 18
    - Pipe fragmentation and extraction 19
    - Pipe loop system 20
    - Miniature pipe system 21
    - Pipe incubation method 21

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EPA Form 2360-4 (4-80)
(PREVIOUSLY CIN. EPA FORM 387)

TYPING GUIDE SHEET

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5. Results and Discussion 22
    Hydride derivatization method 22
    Grignard derivatization method 23
    Analysis of pipe fragment extracts 30
    Miniature pipe system 44
    Pipe loop experiments 51
        Control loop 51
        PVC pipe loop 51
        CPVC pipe loop 54
    Pipe incubation results 57
    Quality assurance testing 62

References 65
Bibliography 67
Appendix A 77
    Sample concentration using XAD-resin 77
    Organic solvent extraction 78
    Flameless atomic absorption 88
    High-pressure liquid chromatography (HPLC) 88
    Thin-layer chromatography (TLC) 90
    Gas chromatography 91
    Mass spectrometry 91
    References 102

BEGIN LAST LINE OF TEXT
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5/8"

PAGE NUMBER
EPA Form 2350-4 (4-80)
(PREVIOUSLY EPA FORM 38?)

TYPING GUIDE SHEET

FIGURES

Number		Page
1	Hodge-type hydride burner	13
2	Separation of hydrides on glass beads	14
3	Separation of hydrides on OV-1	16
4	Gas chromatograms of butylpentyl tins and tetrapentyl tin on an OV-1 column at 200°C	24
5	Mass spectrum of tributylpentyl tin	25
6	Mass spectrum of dibutyldipentyl tin	26
7	Mass spectrum of butyltripentyl tin	27
8	Mass spectrum of tetrapentyl tin	28
9	Chromatogram of compounds leached from CPVC #6, on 3% (w/w) OV-17, 90°C isothermal temperature	31
10	Mass spectrum of the 3.0-minute peak in the chromatogram of CPVC #6	32
11	Mass spectrum of the 3.8-minute peak in the chromatogram of CPVC #6	32
12	Isobutane chemical ionization mass spectrum of CPVC #6 3.8-minute peak	33
13	Chromatogram of dibutyltin-bis-isooctylthioglycolate ester saponification products, on 3% (w/w) OV-17, 90°C isothermal temperature	34
14	Mass spectrum of the 3.2-minute peak in Figure 13	35
15	Mass spectrum of the 4.1-minute peak in Figure 13	35
16	Total ion current chromatogram of the Grignard butylation products of sample #14A	37
17	Total ion current chromatogram of Grignard butylation products of sample #14C	38
18	Total ion current chromatogram of Grignard butylation products of blank sample	39
19	Total ion current chromatogram of Grignard methylation products of sample #14C	40

EPA Form 2350-4 (4-80)
TYPING GUIDE SHEET

Number Page

20 Analysis of extractant water digest of PVC sample #14A by hydride-generation atomic absorption (0.1 mL sample in 100 mL)........ 41

21 Analysis of extractant water digest of PVC sample #14A by hydride-generation atomic absorption (10 mL sample in 100 mL)........ 42

22 Gas chromatogram of isooctyl thioglycolate on 10% (w/w) OV-1, 160°C isothermal temperature (0.5µL/mL in pentane)........ 43

23 Gas chromatogram of aqueous cement solvent standard on a column of 1% SP-1000 on 60/80 Carbopack B at 170°C..... 45

24 Hydride-generation atomic absorption analysis of tap water blank, showing three unidentified organotin species........ 50

25 Standardized organotin chloride concentrations observed in PVC sample #14A pipe loop water samples........ 55

26 Standardized cement solvent concentrations observed in PVC sample #14A pipe loop water samples........ 56

27 Standardized organotin chloride concentrations observed in CPVC #14C pipe loop water samples........ 59

28 Standardized cement solvent concentrations observed in CPVC sample #14C pipe loop water samples........ 60

29 Standardized organotin chloride concentrations observed in CPVC #4 pipe incubation water samples........ 61

A-1 Mass spectrum of dibutyltin bromide chloride and dibutyltin dibromide from hydrobromic acid/benzene extraction of a dibutyltin dichloride water standard..... 80

A-2 Gas chromatogram of a concentrated hydrobromic acid/benzene extract of a dibutyltin-bis-laurylmercaptide water solution........ 83

A-3 Mass spectrum of dibutyltin-bis-laurylmercaptide extraction degradation product........ 84

A-4 Gas chromatogram of dibutyltin-bis-isooctylthioglycolate acetone stock solution........ 85

A-5 Gas chromatogram of a concentrated hydrobromic acid/benzene extract of a dibutyltin-bis-isooctylthioglycolate water solution........ 86

A-6 Gas chromatogram of isooctyl thioglycolate........ 87

A-7 Mass spectrum of dibutyltin dichloride........ 93

A-8 Mass spectrum of tributyltin chloride........ 94

Number		Page
A-9	Mass spectrum of trimethyltin chloride..................	95
A-10	Mass spectrum of dibutyltin dihydride...................	96
A-11	Mass spectrum of tributyltin hydride....................	97
A-12	Mass spectrum of dibutyldimethyl tin....................	98
A-13	Mass spectrum of tributylmethyl tin.....................	99
A-14	Mass spectrum of tetramethyl tin........................	100
A-15	Mass spectrum of tetrabutyl tin.........................	101

EPA Form 2350-4 (4-80)
(PREVIOUSLY EHL EPA FORM 287)

TYPING GUIDE SHEET

TABLES

Number — Page

1 Organotin Reference Compounds.............................. 6

2 Analysis of Water Samples Exposed to Cement Solvent in a Miniature Pipe System.................................... 46

3 Results of Organotin Analyses of Samples from the PVC #14A Pipe Loop.. 53

4 Results of Organotin Analyses of Samples from the CPVC #14C Pipe Loop.. 58

5 Reproducibility of Butyltin Hydride Responses............. 63

6 Accuracy of Observations of Cement Solvents............... 64

A-1 Efficiency of Solvent Extraction of Dibutyltin Dichloride from Water.. 79

A-2 Relative Flameless Atomic Absorption Responses of 1 PPM Standards in Various Matrices............................ 89

EPA Form 2350-4 (4-80)

TYPING GUIDE SHEET

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EPA Form 2250-4 (4-80)
TYPING GUIDE SHEET

SECTION 1

INTRODUCTION

Approximately 800,000 metric tons of polyvinyl chloride (PVC) and copolymer were produced for pipe and conduit applications in 1977. A portion of this was used in potable water supply systems because of cost and handling advantages over other materials, mainly metals (1). Use of PVC and chlorinated polyvinyl chloride (CPVC) pipe for potable water raises the question of whether chemicals of a toxic nature diffuse from the pipe into the water supply, and if so, in what quantities. Organotin compounds used as thermal stabilizers in PVC and CPVC pipe formulations are of particular concern if leached, due to their toxicities.

The types of PVC and CPVC used for pipe are rigid materials with little or no plasticizer. They contain compounds such as thermal stabilizers, lubricants, fungicides, fillers, and pigments to aid in processing and prolong useful life (2). PVC undergoes complete dehydrochlorination at 300°C (3), and partial dehydrochlorination at lower temperatures. Thus, a thermal stabilizer must be added to prevent undue degradation of the material during processing (2). The presence of hydrogen chloride (HCl), or the chloride radical, accelerates the decomposition of PVC and CPVC. An important function of a thermal stabilizer is to react with any chloride formed during processing to eliminate it(4,5). Stabilizers used with PVC and CPVC in the United States are organometallic salts of tin, calcium, zinc, calcium-zinc, and antimony (2). Organotin compounds are the most widely used for stabilizing PVC and CPVC potable water pipe. Specific compounds used include methyl-, butyl-, and octyltin esters, particularly of lauric, maleic, and thioglycolic acids (4). Nine manufacturers have organotin stabilizers accepted by the National Sanitation Foundation (NSF) for use in PVC and CPVC potable water pipe formulations. Organotin stabilizers are used in the range of 0.3 to 1.5 parts per 100 parts resin for PVC pipe and fittings, and in the range of 1.5 to 3.5 parts per 100 parts resin for CPVC pipe and fittings.

Whenever a liquid and solid phase are in contact, there is opportunity for components of the liquid phase to plate out onto the solid, and for components of the solid to be leached into the liquid phase. It is quite possible that potable water could leach compounds from PVC and CPVC pipes, particularly additives that are mixed with the polymer and not chemically reacted with it. Factors influencing the leaching process include pH, temperature, ionic composition of the water, exposed surface area and surface porosity of the pipe material, water solubility of the polymer additives, the ability of these additives to migrate from within the pipe to the surface, and the reactivity of the additives with each other and with the polymer. Organotin

EPA Form 2200-4 (4-80)

TYPING GUIDE SHEET

compounds theoretically react with the polymer during stabilization so that only their reaction products are available for leaching, in the form of alkyl tin chlorides. However, excess stabilizer is usually present in the pipe.

The primary objective of this research was to determine whether or not organotin compounds were introduced into potable water when using PVC or CPVC pipe containing organotin compounds as stabilizers. A secondary objective was to determine the quantities of other selected organic compounds which might be leached from these pipe systems into the water supply. The approach used was to first establish analytical methodology capable of determining the extracted chemicals present at very low levels, and then to incorporate that methodology in a system to quantify the organotins and other compounds in water supplies after contact with PVC and CPVC pipe. The results obtained are a necessary component of the data needed by toxicologists to determine whether or not the use of plastic pipe for potable water distribution presents a health hazard.

SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

1. Alkyltin species were extractable from PVC and CPVC pipes by water. The amount of dimethyltin (as the dichloride) leached from PVC into pH 5 extractant water at 37°C was 35 ppb for day one, and decreased from approximately 3.0 to 0.25 ppb per 24 hours in a biphasic manner from days 2 through 22. The amount of dibutyltin (as the dichloride) leached from CPVC into pH 5 extractant water at 72°C was 2.6 ppb for day one, and decreased from 1.0 to 0.03 ppb per 24 hours, again in a biphasic manner, from days 2 through 21. Both results were obtained when pumping extractant water continually through an 8.9-meter rectangular closed loop of one-inch internal diameter pipe having an inner surface area of 0.71 m^2 (1100 in^2), over a 22-day period, during which time the water was completely removed for analysis and replaced at two- to four-day intervals.

   a. The exact organotin compounds from which these alkyltin species arose were indefinite, although there was evidence that they existed in ionic form in the extractant water.
   b. No evidence of the sulfur-containing part of the stabilizer was found in the extractant water.
   c. The dynamics of the extraction process were not fully resolved, but the rate of decrease at the end of 21 days indicated that detectable amounts (0.005 ppb per 24 hours contact time) of organotin species would be present for long periods of time under normal service.
   d. Experiments should be performed to determine leaching rates at other pH and temperature conditions. Testing should be carried out over longer time periods (6-12 months) to determine whether or not extraction of organotin species is a continuing process.
   e. Future studies should be directed toward determining whether these levels present a human health hazard. Therefore, further analytical work, as outlined in (d), should be performed in conjunction with toxicity testing of the extractant water samples, or equivalent synthetic samples at the low-ppb level.

2. Volatile organic solvents (methyl ethyl ketone, tetrahydrofuran, and cyclohexanone were monitored) used in the sealing cements applied to PVC and CPVC pipe joints continued to leach into water supplies for more than 14 days using the miniature pipe system. The quantities ranged from 10 ppm to 10 ppb during the 15 days of sampling.

3. The hydride-generation methods of Hodge, Braman, and others permitted

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EPA Form 2350-6 (4-80)
TYPING GUIDE SHEET

organotin analysis at concentrations below 0.01 ppb.

   a. Matrix effects were encountered using hydride generation. Although the major effect resulted from chlorine in the sample and was overcome by adding sodium thiosulfate to the sample, considerably more work is needed to understand and control more subtle matrix effects. A single analytical procedure may not be suitable for all sample matrices.

4. The Grignard derivatization method was applicable to the organotin species encountered in water extracts of CPVC pipe when the pentyl derivatives were used, rather than the methyl and butyl derivatives recommended by Meinema.

5. Other conventional methods of concentrating, separating, and identifying the organotin compounds of interest did not prove to be readily applicable. These included high-pressure liquid chromatography, ion-pairing chromatography, flameless atomic absorption, and thin-layer chromatography. Mass spectrometry was useful in conjunction with the hydride and Grignard derivatization methods for identification of various constituents.

SECTION 3

MATERIALS AND INSTRUMENTATION

MATERIALS

Pipe and Stabilizer Samples

During the first month of this research a letter was drafted and directed to three facets of the PVC and CPVC pipe industry, i.e. the pipe fabricators, the compounders, and the manufacturers of tin stabilizers. The purpose of the letter was threefold: first to inform them of our program; second to request samples; and third to solicit publicly-available information on formulations used.

The response to this letter was extremely favorable. As a result of the letter and follow-up contacts, we received 17 pipe samples from eight manufacturers and six resin samples from which some of the pipe samples were formulated. Eight stabilizer samples were received. There were only two negative responses, and 19 manufacturers failed to respond.

Time permitted only two of the pipe samples to be used in pipe-loop experiments. The two samples chosen were representative of widely-used PVC and CPVC pipe compounds. They incorporated primarily dimethyltin- and dibutyltin-bis-isooctylthioglycolate stabilizers, respectively, although stabilizer formulations may contain mixtures of alkyltin isooctylthioglycolates. In fairness to manufacturers, and in accordance with our letter requesting samples, all pipe and stabilizer samples are referred to by code.

PVC and CPVC Schedule 80 gray fittings were used in joining the PVC and CPVC loops, respectively. These fittings met NSF standards. Pieces to be joined were cleaned using a commercial cleaner-primer containing 2-butanone and cyclohexanone. The PVC loop was assembled using a commercial solvent cement containing tetrahydrofuran, 2-butanone, cyclohexanone, N,N-dimethylformamide, and dissolved PVC resin. The CPVC loop was assembled using a similar product containing tetrahydrofuran, 2-butanone, cyclohexanone, and dissolved CPVC resin. The cleaner and cements were purchased locally and met NSF and American Society for Testing and Materials (ASTM) standards. Solvent cement and pipe samples were analyzed by emission spectroscopy prior to use to establish that they contained tin stabilizers.

Organotin Reference Compounds

The organotin reference compounds used in this study and listed in Table 1 were used as received, with the exception of dibutyltin dichloride which was

TABLE 1. ORGANOTIN REFERENCE COMPOUNDS

Compound	Source
Butyltin trichloride	K & K* #9605
Dibutyltin dichloride	K & K #2958
Tributyltin chloride	K & K #19142
Methyltin trichloride	K & K #25293, Alfa§ #71156
Dimethyltin dichloride	K & K 12304
Trimethyltin chloride	K & K 18832
Phenyltin trichloride	K & K #18472
Dibutyltin dihydride	In-house synthesis
Tributyltin hydride	K & K #23707
Tetrabutyl tin	K & K #19200
Tetramethyl tin	K & K #8249
Dibutyl-bis-laurylmercaptide	K & K #22914
Dibutyltin-bis-isooctylthioglycolate	K & K #22887
Dibutyltin-bis-(2-ethylhexanoate)	Eastman+ #10427
Dibutyltin-bis-(2-ethylhexanoate)	NBS‡ #1057b

---

* K & K Rare and Fine Chemicals, Life Science Division of ICN Pharmaceuticals, Inc., Plainview, NY.

§ Alfa Division, Ventron Corporation, Danvers, Massachusetts.

+ Eastman Organic Chemicals, Rochester, NY.

‡ National Bureau of Standards, Washington, D.C.

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recrystallized from hexane prior to use. Methyltin trichloride was the only compound having major impurities. Minor impurities totaling <2% (w/w) were often detected by gas chromatography, and all of the organotin chlorides analyzed by mass spectrometry had detectable organotin bromide contamination. Both samples of dibutyltin-bis-(2-ethylhexanoate) had certified tin contents, but there was no assurance that all the tin existed in the organic form. There is a general lack of certified organotin reference compounds.

Five compounds (listed in Table 1) were used in the preparation of quantitative standards for this study; the three butyltin chlorides (dibutyltin dichloride after recrystallization), dimethyltin dichloride, and trimethyltin chloride. Each of these compounds was analyzed by hydride-generation atomic absorption at a concentration and instrument sensitivity capable of detecting tin and alkyltin impurities at levels $\geq$ 1% (w/w). No such impurities were found and the purity of these compounds was assumed to be 100%. Both samples of methyltin trichloride had large (>10% w/w) dimethyltin and/or trimethyltin impurities, precluding their use as standard compounds since no effective purification method was found.

Aqueous Standards of Tin, Organotin Compounds, and Cement Solvents*

Aqueous standards of inorganic tin were relatively unstable. Braman (6) and others used a 1000 mg/L stock solution of inorganic tin prepared in 10% (v/v) hydrochloric acid with 8% (w/v) citric acid as stabilizer. This stock solution was found to be stable for more than three weeks. Working standards at the ppm level were prepared fresh daily by serial dilution. Braman used 10% (v/v) hydrochloric acid as diluent, but we used 4% (v/v) hydrochloric acid as diluent in our work to minimize the inorganic tin blank. Mineral acids generally have significant concentrations of metallic contaminants, including tin. For this study, 6M redistilled hydrochloric acid (#43602) was purchased from the G. Frederick Smith Chemical Company, Columbus, Ohio. This acid had a very low level of inorganic tin, but had three low-level (<10 ppb) organotin contaminants. It was therefore mainly used for tin analysis.

Aqueous standards of organotin compounds have often been prepared by dilution of high-concentration stock solutions in ethanol (7), acetone, or other water-miscible solvent. There was considerable potential for solvent-induced transformations of the original organotin compound to occur with this method of standard preparation. These transformations generally did not hinder the analysis of alkyltin species, as the tin-carbon bond was quite stable. These transformations did, however, preclude analysis of the anionic portion of the compound.

Aqueous solutions of alkyltin halides in the <0.1 - 10 ppm range were prepared fresh daily by serial dilution of 1000-ppm stock solutions. Water was used as solvent for the methyltin halide stock solutions, while acetone or 95% (v/v) ethanol was used as solvent for stock solutions of the other alkyltin halides. For flameless atomic absorption work, the amount of organotin compound was adjusted to provide a stock solution containing 1000 ppm tin. Stock solutions of alkyltin halides were stable for at least two weeks. A definite cloudiness was immediately noted when aliquots of either the dibutyltin-bis-laurylmercaptide or the dibutyltin-bis-isooctylthioglycolate stock solutions were added to water, indicating that some transformation of these compounds had occurred. One-ppm water solutions of these stabilizers resulted in flameless atomic absorption responses to tin nearly the same as that of a one-ppm water solution of dibutyltin dichloride. All of these solutions were prepared from acetone stock solutions, so the tin was either dissolved or finely dispersed in the stabilizer solutions (see Appendix A, Table A-2).

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*Doubly-distilled water was used for preparing all aqueous solutions.

Aqueous standard solutions containing tetrahydrofuran (Fisher, T-397) and methyl ethyl ketone (Fisher, M-209) were prepared either by direct injection of microliter quantities of solvent into water, or by serial dilution of an aqueous stock solution containing 100 uL of each chemical/100 mL solution. Cyclohexanone (Baker, G032) standard solutions were prepared by direct injection of microliter quantities of solvent into water. None of these compounds had detectable (>1% w/v) impurities when analyzed on gas chromatograph columns packed with either Porapak P or 1% (w/w) SP-1000 on Carbopack B. Their purities were assumed to be 100%.

Preparation of Extractant Water

The extractant water composition was similar to that recommended in the National Sanitation Foundation Standard 14 (8). Each liter contained 111 mg calcium chloride (Matheson, Coleman & Bell, CX170) with hardness equivalent to 100 mg calcium carbonate/L, 84 mg sodium bicarbonate (Matheson, Coleman & Bell, SX0320) as buffer, and 1 mg chlorine (0.5 mL of a stock 2 g chlorine/L solution, prepared by adding 7.65 mL of Chlorox, a commercial 5.25% (w/v) solution of sodium hypochlorite, to 200 mL water). A pH of approximately 5 was obtained by bubbling the solution with carbon dioxide (Linde Bone Dry Grade).

Grignard Alkylation and Hydride Generation Reagents

Methylmagnesium bromide (3M in ether, 87324), n-pentylmagnesium bromide (1.5 - 2.5M in ether, 87296), and phenylmagnesium bromide (3M in ether, 87326) were purchased from Alfa Division, Ventron Corporation, Danvers, Massachusetts, and were used as received. Butylmagnesium bromide was synthesized in-house by reaction of n-butyl bromide (Baker, C878) with magnesium metal. Tropolone (K&K, 19610) was used as received in the extraction process prior to Grignard alkylation.

Sodium borohydride (Sigma, S 9125) contained approximately 0.5% (w/w) magnesium carbonate to minimize caking. The tin content of the 4% (w/v) solution used for hydride generation was reduced by plating onto a carbon cathode rod at 3V while helium was bubbled through the solution, according to the procedure described by Hodge (9). Both the sodium thiosulfate (Baker, 3946) used to eliminate the chlorine interference, and the acetic acid (Mallinckrodt, 2504) used to acidify the sample solution were used as received.

INSTRUMENTATION

Atomic Absorption

A Jarrell-Ash JA 82-270 unit with a Jarrell-Ash FLA-10 Flameless

Atomizer was used for both flameless and hydride-generation analyses. The Jarrell-Ash hollow cathode lamp was obtained through Fisher Scientific (45-463).

Gas Chromatography

A Hewlett-Packard 5730-series gas chromatograph with flame ionization detector and a Hewlett-Packard 3380A integrator were used. All columns were 4-mm internal diameter. A variety of column packings were used throughout the study, including 80/100 mesh Porapak P (Applied Science, 05913), 60/80 mesh Tenax-GC (Applied Science, 04900), 3% (w/w) or 10% (w/w) OV-17 phenylmethylsilicone on 80/100 mesh Gas-Chrom Q (Applied Science, 12740 or 12733), 3% (w/w) SE-30 or 10% (w/w) OV-1 dimethylsilicone on 80/100 Gas-Chrom Q (Applied Science, 12406 or 12730), and 1% (w/w) SP-1000 on 60/80 mesh Carbopack B (Supelco, 1-1815).

High-Pressure Liquid Chromatography

The high-pressure liquid chromatography unit was assembled in-house using components from a variety of manufacturers. It included a Milton Roy Company Controlled Volume mini-Pump, A Rheodyne, Inc. Model 7120 syringe-loading sample injector, and a Laboratory Data Control Spectro Monitor III variable-wavelength ultraviolet absorption detector. Whatman Partisil PXS 5/25 ODS and Waters Associates μBondapak C_{18} (27324) reverse phase columns, and a LiChrosorb Si 60 5μ (Altex 253-33) normal phase column were used.

Thin-Layer Chromatography

Precoated Silica Gel G thin layer chromatography plates were purchased from Applied Science Laboratories (16467). These plates were activated before use by heating at 110°C for 30 minutes according to the manufacturers instructions.

Emission Spectroscopy

A Bausch & Lomb 2-meter Dual Grating Spectrograph (33-83-45) with National Spectrographic Laboratories Spec Power (110-10) arc/spark power supply and Spex Industries (9010) arc/spark stand were used to determine the presence of tin in pipe and stabilizer samples. Data output was on photographic plates. Dispersion was 4 Å/mm. Carbon electrodes were obtained from Ultra Carbon Corporation, Bay City, Michigan.

Mass Spectrometry

The mass spectrometer used in this study was an Associated Electrical Industries MS-30, a double-beam, double-focusing magnetic sector instrument. It was interfaced to a Pye series 104 gas chromatograph via a silicone membrane separator, and coupled to an Associated Electrical Industries DS-30 data system.

SECTION 4

EXPERIMENTAL PROCEDURES

ANALYTICAL METHODS AND QUALITY ASSURANCE

The procedure originally proposed, which would logically be followed in dealing with stable contaminants in an aqueous solution was as follows:

Phase 1. Determine what compounds could be extracted from the plastic pipe by water, and in what quantities. Phase 2. Develop an extraction system and carry out extractions simulating common usage of plastic pipe. Phase 3. Develop and evaluate an analytical system to determine the amounts of extractables from plastic pipes both routinely and precisely.

During the early stages of the research it was determined that Phases 1 and 3 had to be coordinated because the extracted compounds could not be identified by conventional methods and an analytical system could not be developed without knowing what compounds were to be analyzed. Therefore, the problem was redefined and divided into two different tracks which were carried on concurrently. First, an investigation of how organotin compounds are extracted from water was undertaken. Second, methods that had been used previously on organotin compounds were investigated to determine whether they were applicable to this problem.

For analysis of trace organics in water, the organic compounds are often removed from the water by passing the sample through a macroreticular resin (i.e. XAD) or Tenax-GC, which is then stripped with methanol, diethyl ether, or other solvent. By an alternate method, the organics are extracted from water with a small amount of organic solvent, e.g. hexane, as proposed by Grob (10). The organic solutions derived from the resin or extraction procedures are concentrated, generally by evaporation of solvent, to the volumes necessary for direct application of the various instrumental techniques. Although organotin compounds could be extracted by the above-mentioned resins, they could not be removed using organic solvents. Ion formation apparently caused them to become permanently bound. Similar binding characteristics were exhibited when conventional chromatographic techniques were used. Direct organic extraction or analysis of the organotin compounds in the original aqueous medium were the remaining alternatives. Also, the organotin compounds that leached into the water could not be identified directly by conventional means, either because they only existed in an ionic form in the aqueous matrix or because they were changed into such a form during any attempt to remove them for analysis. The former was the reason suggested by Rochow (11) and Van Der Kelen (12). Also, some recent work by Tobias (13) clearly illustrates

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the complex species transformations of methyltin compounds (chloride, hydroxide and oxide conversions) with pH change. The chemistry becomes more complex when changes in temperature and the presence of other ions in solution are considered.

The method of direct analysis of hydride derivatives formed in the water sample as described by Braman (6) and Hodge (9), and the organic extraction and derivatization method used by Meinema (7) were selected for testing and adaptation to the analysis of organotins leached from plastic pipe into water. Neither approach completely determined the form in which the organotins existed in the water sample. Nevertheless, these methods provided some speciation.

Hydride Generation

Two closed-system hydride generation techniques for the detection and quantitation of alkyltin species in environmental samples have been proposed. Braman (6) developed a detector which measured SnH-band emission as the sample was passed through a hydrogen-rich hydrogen-air flame. Hodge (9) developed a method using a hydrogen-rich quartz-tube burner for the atomic absorption analysis of alkyltin hydrides. After generation, the hydrides were frozen out in a trap immersed in liquid nitrogen. They were then separated by boiling point by allowing the trap to warm slowly using either ambient temperature or a resistance heater. In both cases hydrides were generated by the addition of sodium borohydride to a reaction vessel through which helium was being bubbled.

The applicability of the hydride-generation methods of Hodge (9) and Braman (6) to the analysis of both potable water, and water extracts of plastic pipe intended for potable water transport was thoroughly investigated. Our apparatus, which had only minor dimensional differences from that used by Hodge, was as follows:

1. Hydride generator. This was a standard gas washing bottle to which a septum port for addition of sodium borohydride solution was added 1 1/2 - 2" above the base. Bottles of both 125 mL and 250 mL capacity were used in our work for the analysis of 100 mL samples. The sample was purged with helium to volatilize any hydrides formed and to transfer them efficiently to a trap. The smaller headspace volume of the 125 mL bottle proved advantageous in the transfer process.

2. Water trap. A 30-cm, 5.5-mm internal diameter glass U-trap, immersed in dry ice/isopropyl alcohol during analysis, was used to protect the hydride trap from water volatilized during purging of the hydrides. This water trap was only used during analysis of stannane and methyltin species, as the higher-boiling butyltin species were lost in this trap.

3. Hydride trap. A 20-cm, 4-mm internal diameter glass U-tube was packed with 12 cm of 60-70 mesh glass beads with glass wool plugs. This trap was immersed in liquid nitrogen to collect hydrides purged from the hydride generator. The liquid nitrogen was then removed

and the trap allowed to warm to room temperature to release the trapped hydrides according to their boiling points. The trap had to be immersed in an ∿80°C water bath in order to release tributyltin hydride.

4. Hydride burner. The burner consisted of a small Vycor tube positioned in the atomic absorption spectrophotometer so that radiation from the hollow cathode lamp passed down the length of the tube (Figure 1). At the midpoint of this tube, air plus helium and sample entered through lines at the front, and hydrogen entered through a line at the rear. These gases mixed at the center of the tube and travelled to its ends, where they were burned in small flames to produce atomic tin which was then quantitatively determined by the magnitude of its absorbance at 224.6, 235.5, or 286.3 nm.

The procedure for analyzing a sample was as follows:

1. Gas flows were established at 70 mL/minute for helium, 330 mL/minute for hydrogen, and 200 mL/minute for air. The burner flames were lit and the atomic absorption unit was optimized at one of the tin wavelengths.
2. A 100-mL aqueous sample was placed in the hydride generator.
3. 1 mL of 2 N acetic acid was added.
4. The hydride generator was attached to the sampling train and purged with helium to expel air from the system.
5. The hydride trap was immersed in liquid nitrogen and timing was started, while continuing the helium purge. After 4 minutes 35 seconds, 1 mL of 4% (w/v) sodium borohydride was added over a 25-second period.
6. Hydrides were purged from solution onto the hydride trap for 5.0 minutes after addition of sodium borohydride ended.
7. The liquid nitrogen was removed and the hydrides were allowed to evolve from the trap.

Figure 2 shows the separation of stannane, and methyl-, butyl-, and phenyltin species. There was baseline separation of stannane (an impurity at ∿0.1 ppb) and methyltin trihydride, but slight overlap of dimethyltin dihydride and trimethyltin hydride peaks. This separation was achieved using the 12-cm glass bead trap. Separation of stannane and methyltin trihydride appeared to be somewhat better than that reported in Hodge's publication (9), but this may be deceiving due to the comparatively small peaks. Separation of the di- and trimethyltin hydrides was almost identical to that reported by Hodge. The minimum detectable level of dimethyltin dichloride was well below 0.05 ppb in our work. This was similar to the detection limit of 0.5 ng (as dimethyltin dichloride) reported by Hodge (9), but well above the detection limit of 0.65 pg (as Sn) reported by Braman (6).

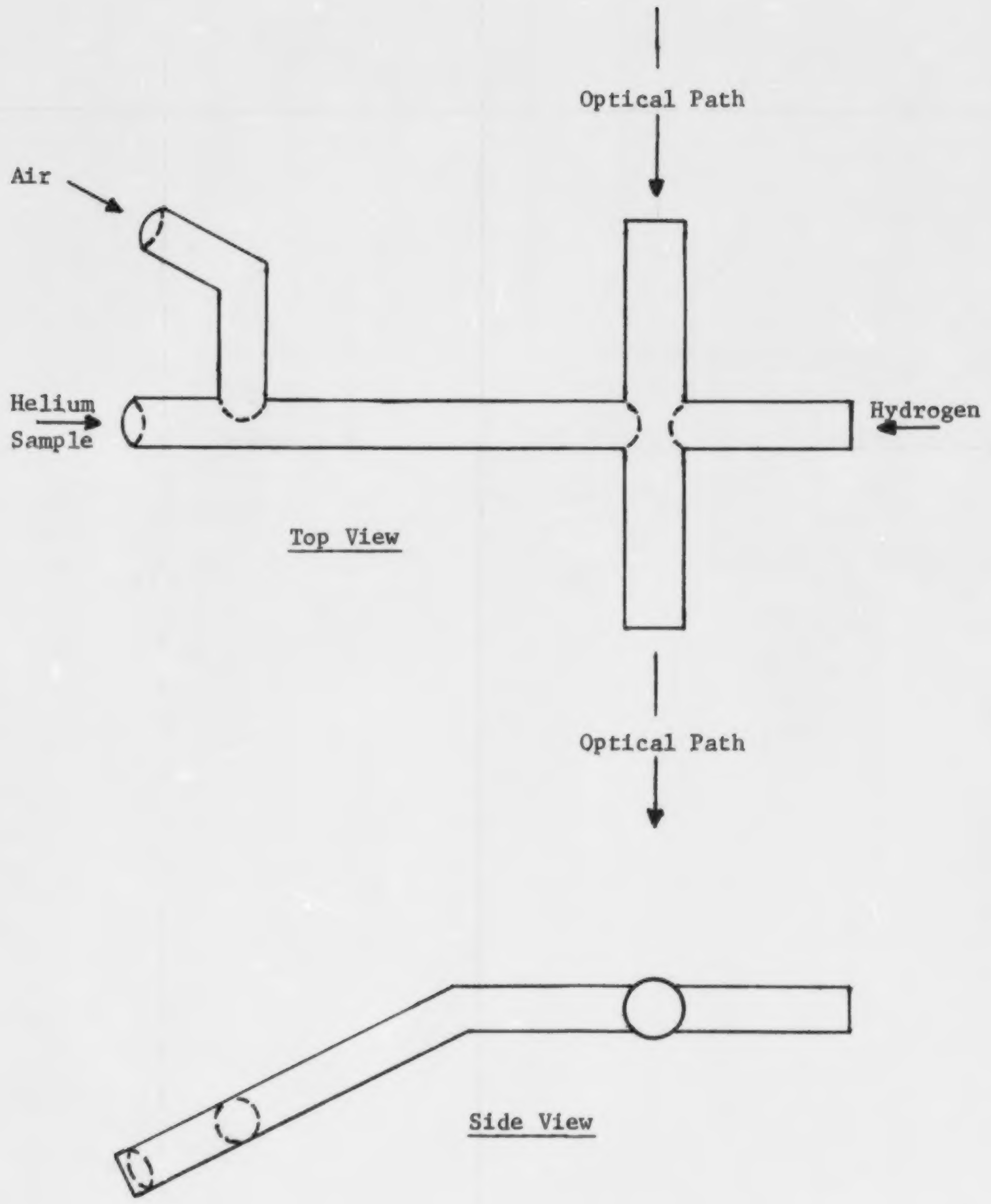
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Figure 1. Hodge-type hydride burner.

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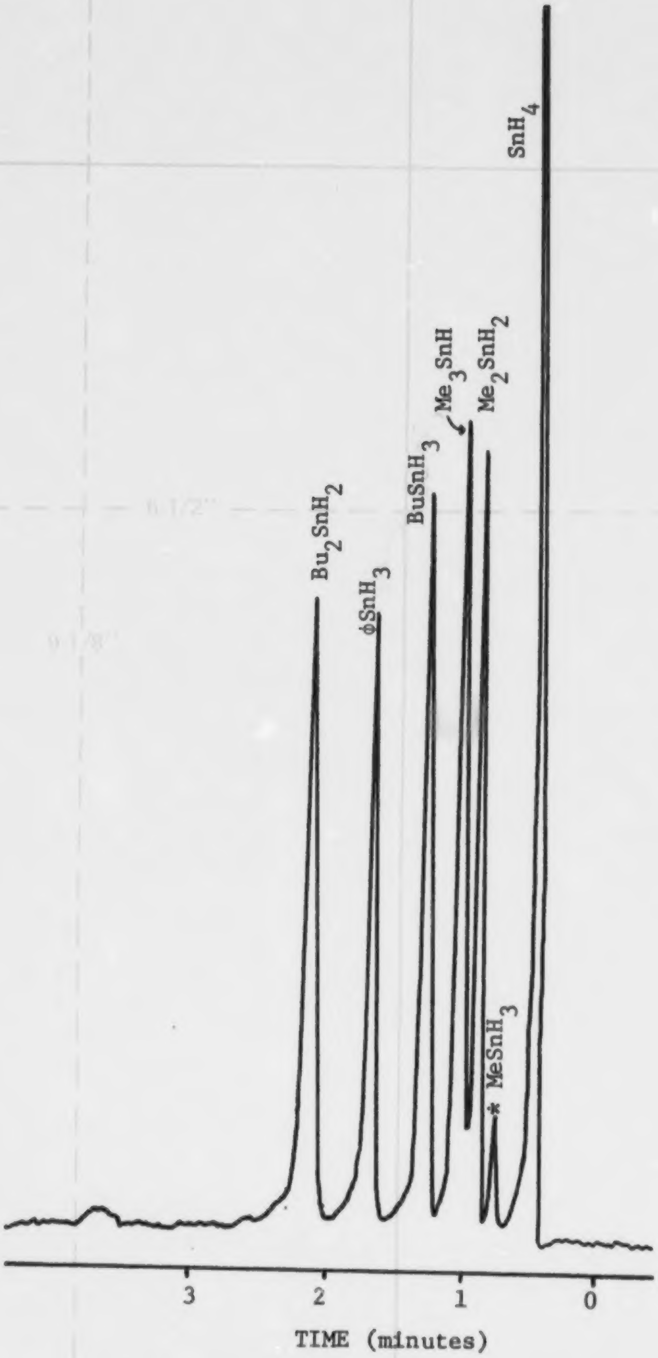

Figure 2. Separation of hydrides on glass beads.
(* Me is methyl, Bu is n-butyl, ϕ is phenyl)

Further investigation of alternative packing materials for the hydride trap was conducted to improve the separation of organotin hydrides. The use of 18 cm of 10% OV-1 on 80/100 mesh Gas-Chrom Q improved separation of methyltin hydrides. After the methyltins eluted, the trap was heated to 145°C to elute the di- and tributyltin hydrides. The separation of the hydrides on OV-1 is shown in Figure 3.

Both standard calibration curves and the method of standard additions were used with the hydride-generation atomic absorption technique. Each calibration point for a standard curve was generated by adding a measured volume of aqueous alkyltin halide standard solution, (prepared by serial dilution of an ethanol stock solution) directly to a hydride generator containing a sufficient volume of doubly-distilled water to make a total volume of 100 mL. The resulting solution was then analyzed according to the hydride-generation atomic absorption procedure. Calibration curves were linear over an approximately 20-fold concentration range which varied with the instrument gain. The lowest range used in this work was 0.05 - 1.0 ppb. Results of triplicate analyses at the same organotin concentration in distilled water generally varied by less than 10%.

Calibration curves were prepared during method development, but due to suspected matrix effects the method of standard additions was selected for quantitative organotin analysis. Duplicate or triplicate analyses of the sample and each addition were performed. Standard aqueous organotin solutions for addition were again prepared by serial dilution of an ethanol stock solution.

Grignard Alkylation

Grignard alkylation is one of the classic reactions of organic synthesis. It involves addition of an alkyl group to a compound through an alkylmagnesium halide intermediate. Grignard butylation and methylation were applied by Meinema (7) to produce tetraalkyltin compounds from various undefined alkyltin species in the aqueous environment. The reaction worked especially well for alkyltin halides, which were used to prepare tetraalkyltin standards. Other alkyltin compounds should react directly, or after addition of acid since tin bonds with elements other than carbon are easily cleaved.

Although initial analyses of butylated water extracts of PVC and CPVC pipe showed considerable promise, they also suffered from the disadvantage that tetrabutyltin derived from inorganic tin could not be distinguished from tetrabutyl tin derived from butyltin stabilizer. Since the use of pentyltin compounds as stabilizers had not been reported, we prepared pentyltin derivatives instead of butyltin derivatives.

An interfering gas chromatographic peak coeluted with the dibutyltin derivative due to a derivatization by-product of the complexing agent tropolone. To overcome this problem, a two-step extraction was developed. First, an extraction of the hydrobromic acid-acidified water sample with benzene was used to recover dibutyltin (Bu_2Sn^{++}) and tributyltin (Bu_3Sn^{+}) species. The water sample was then extracted with benzene containing 0.05% (w/v) tropolone to recover the monobutyltin ($BuSn^{+++}$) and inorganic tin species. The two

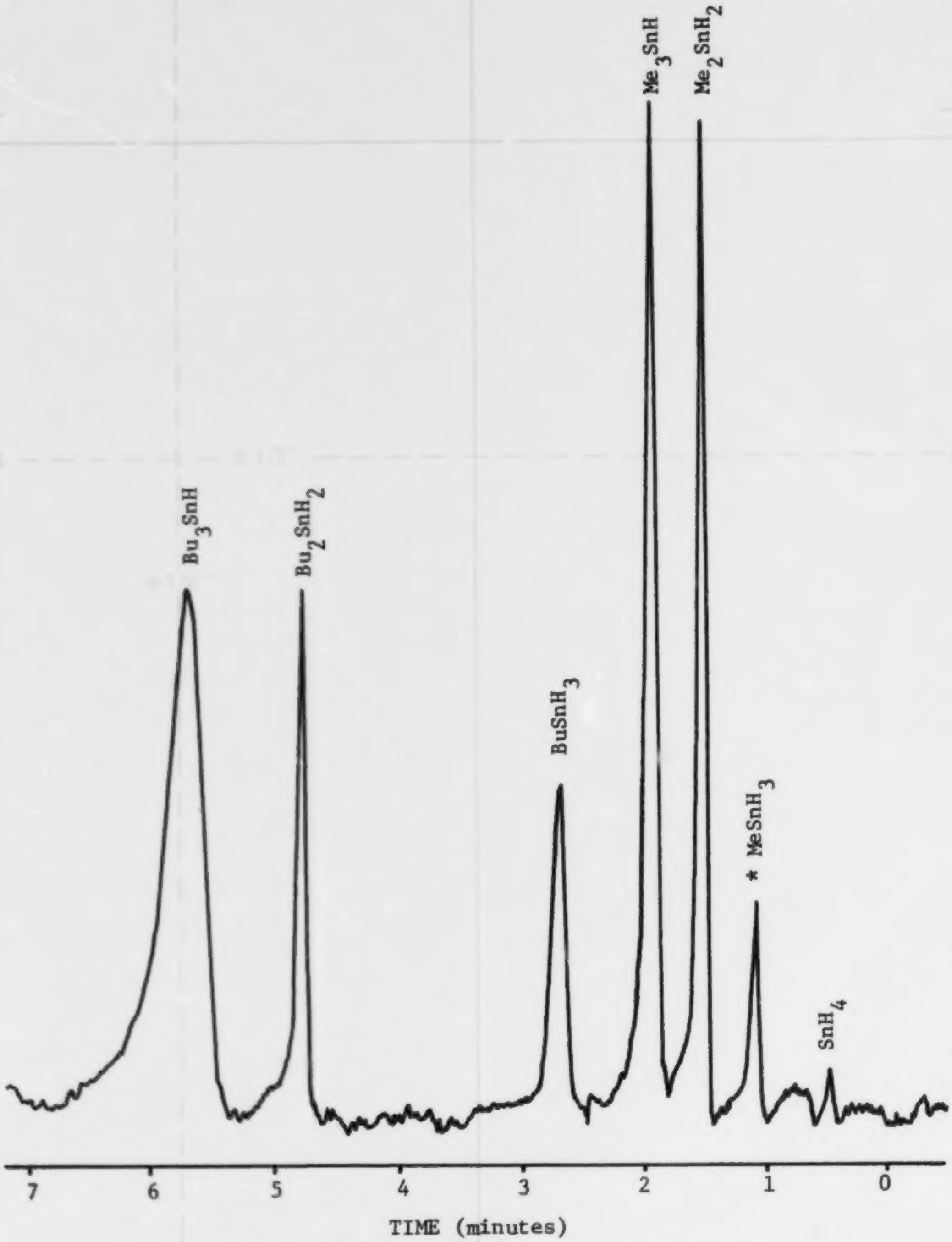

Figure 3. Separation of hydrides on OV-1.
(* Me is methyl, Bu is n-butyl)

extracts were derivatized separately. The procedure was as follows:

1. Solvent extraction

   a) A 250-mL water sample was acidified with 5.0 mL of 48% (w/v) hydrobromic acid, shaken, and allowed to stand for at least 15 minutes.

   b) The acidified water was extracted with two 25-mL aliquots of benzene and the 50-mL extract (I) was set aside for derivatization of dibutyltin and tributyltin species.

   c) The water was then extracted with two 25-mL portions of benzene containing 0.05% (w/v) tropolone and this extract (II) was set aside for derivatization of monobutyltin and inorganic tin species.

2. Derivatization via Grignard reaction

   a) The Grignard reaction apparatus was assembled, and dried by flaming while purging with dry nitrogen.

   b) The extract (I and II separately) was transferred to a separatory funnel.

   c) A 3.0-mL aliquot of Grignard reagent (3.1 M pentylmagnesium bromide in ether) was added to the reaction flask and the extract from the separatory funnel was allowed to flow into the flask while the reaction mixture was slowly stirred. The reaction was allowed to proceed for 30 minutes.

   d) The reaction was stopped by slowly adding 25.0 mL of 1 N sulfuric acid to the flask.

   e) The organic and aqueous layers were allowed to separate.

   f) The aqueous layer was extracted with 25 mL benzene (or benzene containing 0.05% (w/v) tropolone) and the organic layers were combined.

   g) The volume was adjusted to 75 mL with the appropriate solvent.

3. Chromatography

   a) A 5.0-μL aliquot was chromatographed on a column of 10% (w/w) OV-1 on Gas-Chrom Q.

   b) The column was held at an isothermal temperature of 90°C for two minutes and then programmed to 200°C at 16°/minute.

   c) Nitrogen carrier gas and flame ionization detection were used.

The limit of detection of the Grignard alkylation technique, corresponding to approximately 1.5-3 ug alkyltin species in 1 L water, was not as low as that of the hydride-generation atomic absorption method. However, the Grignard alkylation method provided a sample suitable for analysis by mass spectrometry, allowing verification of the presence of alkyltin species.

The Grignard alkylation method was primarily used in this study to confirm the presence of an alkyltin species. Quantitative analysis was affected by the efficiency of extraction of alkyltin species from water into a solvent suitable for carrying out the derivatization reaction, and by the efficiency of derivatization. If the appropriate pure tetraalkyltin compound was available, both efficiencies could be determined; first by derivatizing a known amount of corresponding alkyltin chloride and then by adding the alkyltin chloride to water and carrying out the extraction and derivatization. If the appropriate pure tetraalkyltin compound was not available, a standard curve had to be prepared by derivatizing known amounts of alkyltin chloride. The derivatization efficiency was then assumed to be the same for samples and standards.

Quality Assurance

Certain design goals for developing analytical methodology and laboratory scale pipe extraction systems were specified in the original proposal. Since several of these are related to quality assurance, they are itemized here.

1. To the greatest extent possible, the system should be specific for individual compounds (as opposed to classes of compounds). If this is not possible, the compounds that are included in a specific analysis need to be well defined.

2. The limits of detection should be as low as possible, and the factors that determine these limits should be known.

3. The accuracy and precision of the results should be established and the factors affecting these be defined.

4. Potential interferences, especially of a chemical nature, should be determined and, to the greatest extent possible, eliminated.

5. The procedures should be transferable from laboratory to laboratory with a minimum effect on the specificity and accuracy.

6. The method should be economically feasible, and use existing equipment, as opposed to new equipment. The time expended per sample should be established and minimized.

While some organotin compounds could be readily analyzed, no suitable compound-specific analytical method was found for those tin compounds involved in this research. It was therefore necessary to convert the intractable compounds into some measureable form, even if some speciation information was lost in the derivatization process. The two derivatization reactions suitable for use on many organotin compounds were hydride generation and Grignard alkylation.

To insure accuracy and reproducibility of quantitative results, quality assurance samples were run in the same manner as the pipe extracts. Quality assurance samples were prepared in the same concentration range as the samples by an individual not directly involved in the analysis. One quality assurance sample was run for approximately every 10 samples quantitatively analyzed.

PIPE EXTRACTION SYSTEMS

Four extraction systems were used for the purpose of determining the amounts of organotin and other compounds leached from PVC and CPVC pipe into potable water. First, during method development, fragmented pipe samples were digested with extractant water in order to obtain high surface-to-volume ratios, resulting in higher organotin concentrations than would be encountered in the field. Second, extractant water was continuously pumped through an 8.9-meter rectangualr closed loop of one-inch internal diameter pipe having an inner surface area of 0.71 m^2 (1100 in^2), maintained at constant temperature. This system was used to provide sequential samples over a 22-day period, during which time the extractant water was completely removed for analysis and replaced at two- to four-day intervals. Third, a miniature pipe system attached to a laboratory faucet was used primarily to study the fate of the solvents incorporated in cements used to join segments of pipe. Fourth, incubation of short lengths of pipe with extractant water served as a convenient method to study changes in leach rates as experimental parameters were varied. This simplified dynamic extraction system is being used by Romulo Aquino as part of his dissertation research, to determine and characterize the migration of stabilizer or stabilizer reaction products when temperature, pH, ionic strength, and leaching time are varied.

Pipe Fragmentation and Extraction

Fragmented pipe samples were used to provide a large surface area for determining what compounds were water extractable. One- to two-inch internal diameter pipe was sawed into four-to six-inch lengths and cleaned before fragmenting. To remove oils, dirt and labelling dyes the pipe samples were washed with detergent (Dreft) for the minimum length of time required to remove obvious contaminants, rinsed under running tap water, and then rinsed three times with doubly-distilled water. The plastic was fragmented by freezing it in liquid nitrogen, wrapping it in clean duck canvas, and hammering on a hard supporting surface. This process resulted in irregularly-shaped, 0.35-cm thick pieces, 0.25 to 1.5 cm in length and width. The fragments were rinsed under running tap water to remove fines and canvas fibers. Final rinses were done using distilled and doubly-distilled water. About 400 grams of pipe fragments were placed in a 500-mL Pyrex bottle which was then filled with extractant water (approximately 200 mL). A 5-cc air space was left for the expansion of bottle contents on heating. Each bottle was sealed with a ground glass stopper. The bottles were previously cleaned by washing with detergent (Dreft), rinsing under running tap water, wetting the inside surface with 1:1 nitric acid and waiting at least 5 minutes, rinsing under running tap water, wetting the inside surface with 1:1 hydrochloric acid and waiting at least 5 minutes, rinsing under running tap water, and finally rinsing three times with doubly-distilled water. A blank, consisting of a bottle filled only with extractant water, was run with each set of fragmented pipe samples.

Pipe Loop System

Several design criteria were considered important for the pipe-loop system. First sufficient pipe surface had to be used to allow quantitative analysis of the extractant water over a period of several weeks at organotin concentrations well within the calibration range of the chosen analytical method. Second, the extractant water used had to simulate the pH range and temperature spectrum found for potable water. Because of time constraints, only pH 5 extractant water was used. Extractant water temperatures of 37°C and 72°C were chosen for the PVC and CPVC loops, respectively, because PVC pipe was used for cold-water delivery and CPVC pipe was used for hot-water delivery. Third, the extractant water had to be dynamic because in actual usage, there is an intermittent or continuous flow of water. Fourth, the extraction system had to be designed to avoid introducing organic or organometallic compounds into the water except as extractable from the pipe components. Therefore, mechanical pumps with lubricants, joints, or connectors using other plastics or sealants had to be used very cautiously, with control runs to establish whether such external components contributed contaminants.

The basic component of the system was a 1.71-m (5.6-foot) by 2.74-m (9-foot) rectangular closed loop of one-inch internal diameter pipe having an inner surface area of 0.71 m^2 (1100 in^2). The loop of 8.9-m (29.2-foot) total length was formed using conventional NSF-accepted elbows and solvent cement as described in the Materials and Instrumentation section. Test water was circulated in the loop by a centrifugal pump (Process Controls Co., Livonia, MI 48152. Pump: Dayton Model 6K122. Pump head: Liquiflo; Warren, NJ 07060) having only wetted stainless steel and Teflon parts.

A galvanized pipe loop of the same length was mounted adjacent to the plastic loop and utilized an identical pump. Galvanized pipe was selected over glass or copper for the control loop for several practical reasons. Glass would have had to be special ordered and, of course would have been rather fragile. It would have had to be cemented into the system. Since copper is too soft to be threaded, it would have had to be soldered into the system. The copper used in the manufacture of water pipe may be an alloy, containing tin. Galvanized pipe has previously been used extensively for potable water. Since it was inexpensive, and could be threaded, it could be used in the system without danger of introducing cement contaminants.

Each loop was filled and drained by means of a fill tube that fit directly into an access port at the bottom of the pump head. This port was the lowest point in the system. Another port at the top of the pump head, the highest point in the system, served as a vent and an overflow indicator to signal when the loop was full. Extractant water volumes required to fill the control, PVC, and CPVC loops were 4.8, 4.1, and 3.9 liters, respectively. Volume differences probably reflect variations in the nominal internal diameters of the pipes. The loops were housed in a controlled-temperature heated test chamber, built of sheets of polystyrene insulation. Heating

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elements were incorporated to heat the chamber to 37°C when testing the PVC loop and 72°C when testing the CPVC loop.

Miniature Pipe System

A report by Wang and Bricker (14), stating that cement solvents could be detected in water six to eight months after installation of a PVC pipe system, led us to set up a miniature pipe system to address this problem specifically. The system was attached to a laboratory faucet and was assembled using a galvanized fitting, two gray PVC connectors, four gray PVC elbows, three 0.102-m (4-inch) pieces of PVC sample #9A, and two 0.40-m (16-inch) pieces of PVC sample #14A. The last component of the system was a brass gate valve positioned over a sink. There were 10 solvent-cemented joints in this 1.22-m (48-inch) miniature pipe system. The inner surface area of the plastic was approximately 0.1 m^2 (151 in^2), and the volume of the system was approximately 600 mL. The NSF-accepted solvent cleaner-primer and solvent cement, described in the Materials and Instrumentation section, were used.

When the gate valve was closed, water resided in the system under normal line pressure. When the water was turned off at the faucet, the gate valve could be opened and water from the system collected in a Pyrex bottle, undiluted for an analysis, after a known residence time. Samples were taken periodically over a 2-week period after 4- to 20-hour residence times in the system at normal line pressure. At all other times, water flowed through the system at approximately 4 L/minute. Water to serve as a blank could be drawn from the same line using the faucet at the sink.

Pipe Incubation Method

One-inch PVC or CPVC pipe was cut into 2-inch lengths, placed in a widemouth Pyrex jar, and covered with extractant water with no headspace in the container. The amount of pipe and water was such that there was 4 mL of water per square inch of exposed pipe surface, as recommended by NSF in their standard testing protocol. Incubation was carried out at 25°C with continuous shaking for periods of time up to 168 hours. The water was removed for analysis and replaced with fresh water every 24 hours, unlike the pipe loop system where the water was removed for analysis and replaced at 48- to 72-hour intervals.

Extraction using this method took place over the entire pipe surface, although the volume-to-surface area was approximately the same as in the pipe loop (4 mL water per square inch of exposed surface). Although the extractant water was agitated, it did not encounter the high-speed pumping action encountered by water in the pipe loop. One set of extractions on CPVC sample #4 using pH 5.0 extractant water at room temperature (25°C) was carried out. The formulation of CPVC sample #4 was thought to be identical to that of CPVC sample #14C which was used in the pipe loop.

SECTION 5

RESULTS AND DISCUSSION

The compounds of analytical interest in this research problem were primarily alkyltin-bis-laurylmercaptides and alkyltin-bis-isooctylthioglycolates. These are the most common organotins used as stabilizers, and it is these, or their reaction products, that are of interest to the environmental toxicologists. Prior studies by others indicated that during the PVC or CPVC extrusion process, organotin compounds separate at the tin atom. The heat-liberated chloride reacts to form the alkyltin chloride and the sulfur containing portion of the stabilizer replaces the chloride in the polymer chain. Therefore, analytical techniques for determining ppb (or sub-ppb) levels of unreacted stabilizer and the liberated reaction products in water were required.

Considerable time and effort were expended investigating conventional analytical procedures to determine their applicability to this research. Both column concentration and solvent extraction methods were explored to see if they could be used to remove and concentrate various organotin species from water. Likewise, the detection and characterization of these compounds by atomic absorption, colorimetric analysis, chromatography, and mass spectrometry were explored. A summary of this portion of the research will be found in Appendix A. The most promising methods for analyzing the water extracts from PVC and CPVC pipe appeared to be hydride derivatization followed by atomic absorption analysis of the separated derivatives, and Grignard derivatization followed by gas chromatography and/or mass spectrometry.

HYDRIDE DERIVATIZATION METHOD

After evaluating the hydride-generation atomic absorption method with synthetic samples and the extracts of fragmented PVC and CPVC pipe, the procedure was judged to be suitable for the analysis of both methyltin and butyltin species. Both trapping methods for collecting the hydrides (glass beads or OV-1 packing) were used in analyzing the water samples. The use of OV-1 packing in the collection trap resulted in a better separation of the methyltin hydrides but required heating to 145°C for removal of the butyltins.

During analyses of the samples from the CPVC pipe loop, a significant problem arose using this method. Alkyltin species were not found in the expected concentration range. Furthermore, there was a greatly reduced response to known amounts of these species when added to the water samples prior to analysis. The loss was attributable to a previously-unobserved matrix effect of freshly-prepared extractant water. The problem was traced by analyzing standards in the extractant water with one or more of its various additives omitted. No effect was noted with the omission of sodium bicarbonate and calcium chloride. A substantial improvement (complete recovery in most cases) occurred when the chlorine (added in the form of sodium hypochlorite) was omitted, and a partial improvement occurred when the carbon dioxide was omitted. Further testing identified chlorine as the major interference. It was further determined that the suppression effect of the chlorine was removed by adding sodium thiosulfate as a dechlorinating agent. The chlorine in the water may affect this analytical procedure in one of two ways. First, it may compete for sodium borohydride, decreasing its availability for reaction with the organotin species. However, this appears improbable since the amount of sodium borohydride added was about three orders of magnitude in excess of what could be tied up by the chlorine. A more probable explanation was that the chlorine reacted with the organotin species in a manner making them unreactive to hydride formation. Experiments were carried out to verify that the addition of sodium thiosulfate in a stoichiometric amount to remove the 1 mg/L of chlorine eliminated the problem for dimethyltin dichloride and the three butyltin chlorides. Known standards of the four compounds and metallic tin were run in triplicate in both doubly-distilled water and the extractant water, treating the latter with 0.7 mL of 0.1% (w/v) sodium thiosulfate solution. When the t test was applied at the 95% confidence level, the mean responses of the organotins in doubly-distilled water and in extractant water (dechlorinated) were statistically similar, except for tin. The response of the stannane peak was considerably reduced in the presence of sodium thiosulfate. Subsequent to these findings, all analyses involving the hydride-generation method were preceded by the dechlorinating process.

GRIGNARD DERIVATIZATION METHOD

Although initial analyses of butylated water extracts of PVC and CPVC pipe showed considerable promise, they also suffered from the disadvantage that tetrabutyl tin derived from inorganic tin could not be distinguished from tetrabutyl tin derived from butyltin stabilizer. Since the use of pentyltin compounds as stabilizers has not been reported, we prepared pentyltin derivatives instead of butyltin derivatives.

Gas chromatograms of the three butylpentyl tins and tetrapentyl tin, shown in Figure 4, were obtained using a 3-foot, 4-mm internal diameter column packed with 10% (w/w) OV-1 and held at an isothermal temperature of 200°C. Mass spectra of these compounds, Figures 5-8, show several common ions (at mass-to-charge ratios of 179,193,249, and 263) which could be used for specific ion monitoring. Molecular ions did not appear in the electron impact spectra, but a fragment ion at the molecular ion minus one alkyl chain was always present.

An aqueous solution containing 10 ppm (as Sn) of each of the three butyltin chlorides was prepared from an ethanol stock solution. A 250-mL aliquot was acidified with hydrobromic acid, extracted with benzene containing 0.05% (w/v) tropolone, derivatized using the pentylmagnesium bromide reagent, and re-extracted to give a final volume of 75 mL. The concentration of each

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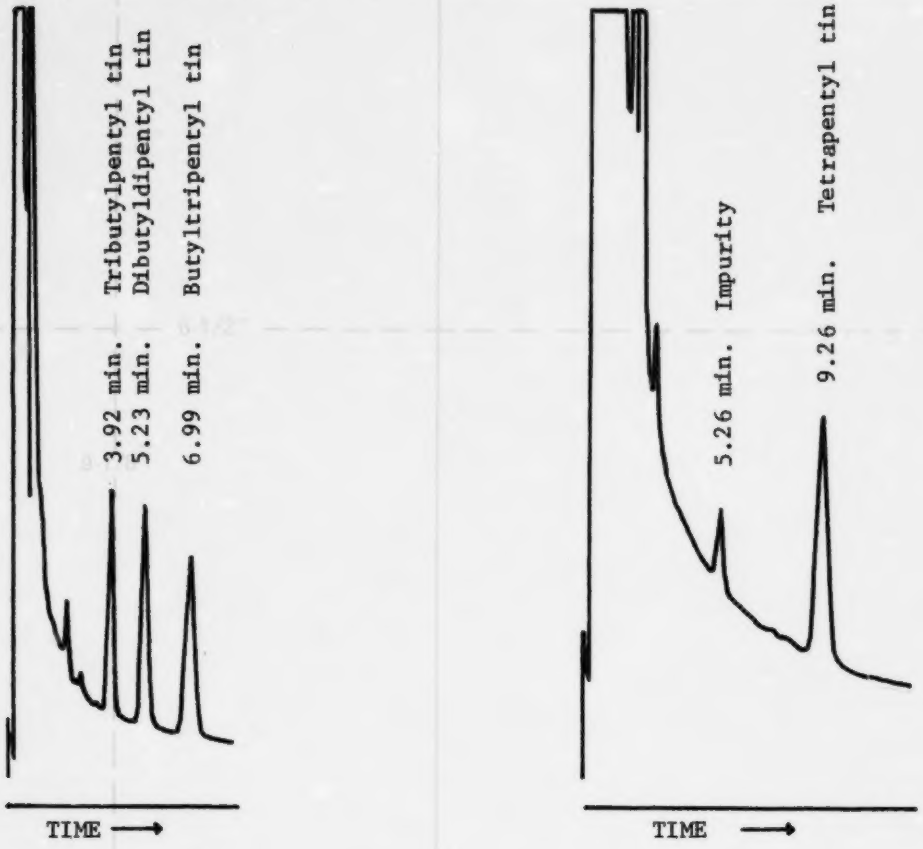

Figure 4. Gas chromatograms of butylpentyl tins and tetrapentyl tin on an OV-1 column at 200°C.

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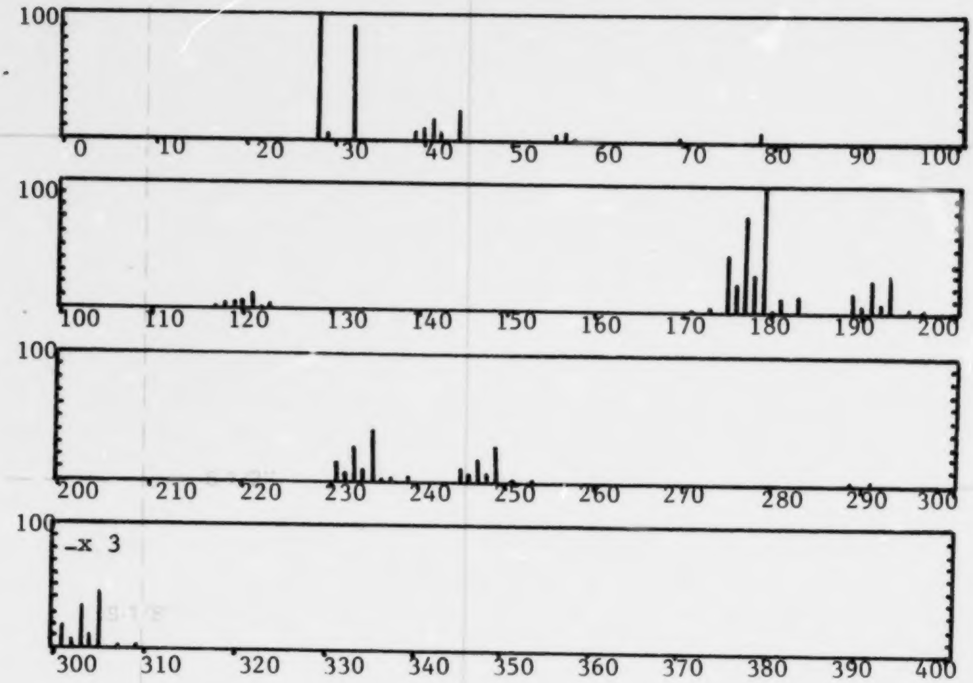

Figure 5. Mass spectrum of tributylpentyl tin.

Explanation: Calculated versus observed isotope abundances are included to aid in determining the quality of the spectrum.

Mass	Assignment	Relative Abundance	
		Calculated	Observed
301	Butyl$_2$ Pentyl ^{116}Sn	0.44	0.37
303	Butyl$_2$ Pentyl ^{118}Sn	0.73	0.73
305	Butyl$_2$ Pentyl ^{120}Sn	1.0	1.0
307	Butyl$_2$ Pentyl ^{122}Sn	0.14	0.05
309	Butyl$_2$ Pentyl ^{124}Sn	0.18	0.05

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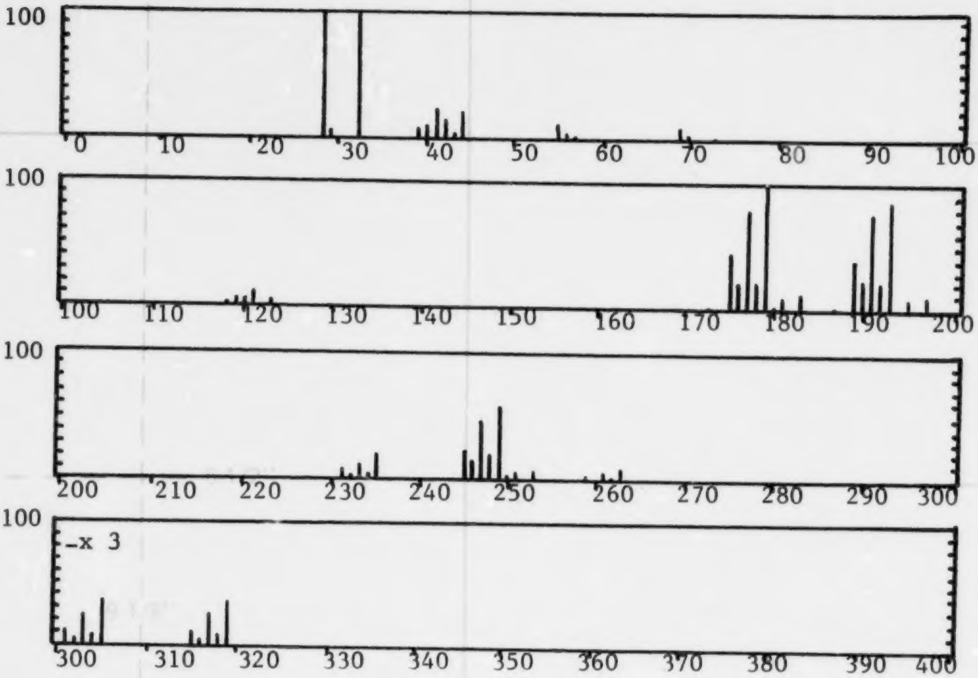

Figure 6. Mass spectrum of dibutyldipentyl tin.

Explanation: Calculated versus observed isotope abundances are included to aid in determining the quality of the spectrum.

Mass	Assignment	Relative Abundance Calculated	Relative Abundance Observed
315	Butyl Pentyl$_2$^{116}Sn	0.44	0.31
317	Butyl Pentyl$_2$^{118}Sn	0.73	0.73
319	Butyl Pentyl$_2$^{120}Sn	1.0	1.0

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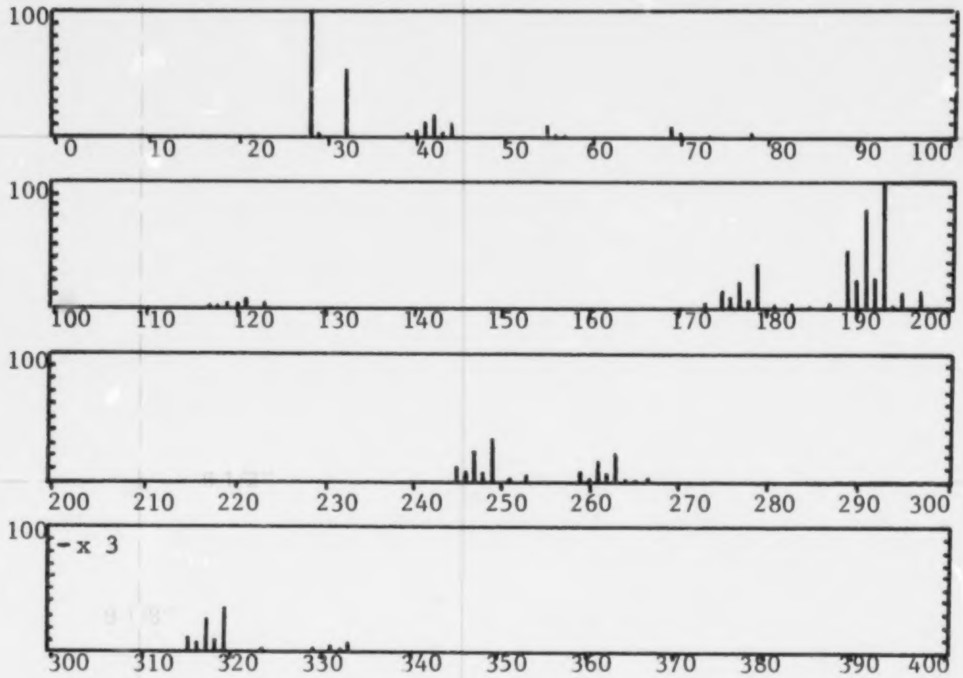

Figure 7. Mass spectrum of butyltripentyl tin.

Explanation: Calculated versus observed isotope abundances are included to aid in determining the quality of the spectrum.

Mass	Assignment	Relative Abundance Calculated	Relative Abundance Observed
315	Butyl Pentyl$_2{}^{116}$Sn	0.44	0.30
317	Butyl Pentyl$_2{}^{118}$Sn	0.73	0.74
319	Butyl Pentyl$_2{}^{120}$Sn	1.0	1.0
329	Pentyl$_3{}^{116}$Sn	0.44	0.30
331	Pentyl$_3{}^{118}$Sn	0.73	0.61
333	Pentyl$_3{}^{120}$Sn	1.0	1.0

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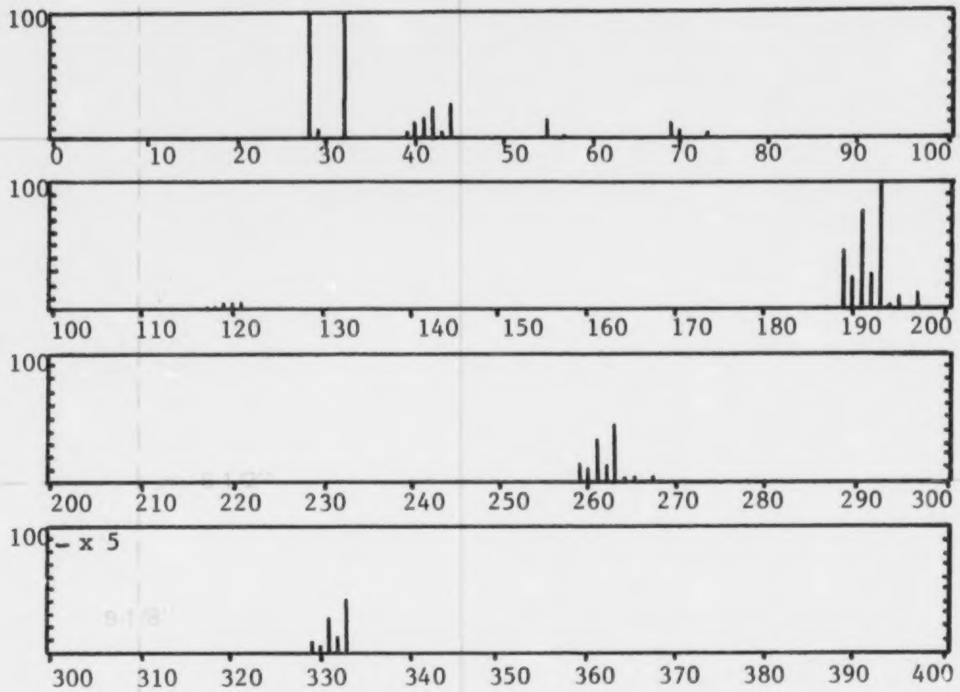

Figure 8. Mass spectrum of tetrapentyl tin.

Explanation: Calculated versus observed isotope abundances are included to aid in determining the quality of the spectrum.

Mass	Assignment	Relative Abundance Calculated	Relative Abundance Observed
259	$Pentyl_2{}^{116}Sn$	0.44	0.36
261	$Pentyl_2{}^{118}Sn$	0.73	0.76
263	$Pentyl_2{}^{120}Sn$	1.0	1.0
329	$Pentyl_3{}^{116}Sn$	0.44	0.22
331	$Pentyl_3{}^{118}Sn$	0.73	0.64
333	$Pentyl_3{}^{120}Sn$	1.0	1.0

component in the final extract was 33.3 ppm (as Sn). Calibration curves constructed from observations of standards with Sn concentrations in the ranges 0-20 ppm and 0-5 ppm showed good linearity over two orders of magnitude. The detection limits (expressed as Sn) for butylpentyl tins and tetrapentyl tin were ~15 and 30 ug, respectively, in the 75-mL benzene extract or 60 and 120 ppb, respectively, in the 250-mL sample. If the extract was concentrated tenfold, the corresponding detection limits were ~ 1.5 and 3.0 ug in the 7.5 mL extract or 6 and 12 ppb in the 250-mL sample. Analyses of 7.5-mL concentrated extracts of 1-L samples could conveniently afford butylpentyl tin and tetrapentyl tin detection limits of ~1.5 and 3.0 ppb, respectively (as Sn).

During these studies some difficulty was encountered due to derivatization of the tropolone used to increase extraction efficiency. Two large impurity peaks eluting just after the solvent (Figure 4), before 3 minutes, did not interfere. However, a series of smaller contaminants did often appear. Peak area discrepancies and mass spectrometry have confirmed that one of these smaller contaminants coeluted with dibutyldipentyl tin. Thus the 5.23-minute peak of dibutyldipentyl tin, shown in Figure 4, coeluted with the 5.26-minute impurity peak shown in the tetrapentyl tin chromatogram of the same figure. This interference was due to a derivatization by-product of the tropolone complexing agent, which was added to benzene to aid in solvent extraction of the tin and organotin species. A modification of the Meinema (7) procedure, detailed in the Experimental Procedures section, overcame this problem. The modified procedure allowed gas chromatography to be used as a quantitative tool. Recoveries of butyltins in this work were approximately 80%, and were similar to the recoveries reported by Meinema.

An aqueous solution containing 10-15 ppm (as Sn) each of the three methyltin chlorides was prepared and a 250-mL aliquot was extracted and derivatized according to the previously-described procedure. When chromatographed on a 3-foot, 4-mm internal diameter, 10% (w/w) OV-1 column held at 80°C for 4 minutes, then heated at 16°/minute to 200°C, only one peak different from the blank was observed. Since butyltin species are not very water soluble but are still moderately difficult to extract from water solution, it was reasonable to suspect that the very water soluble methyltins might be even more difficult to extract. Meinema did not study extraction of methyltin species. No data were available for determining extraction and/or derivatization efficiencies. The aqueous solution remaining after extraction was analyzed by the hydride-generation atomic absorption technique. High levels of methyltins were detected, thus demonstrating qualitatively and semiquantitatively that the extraction efficiencies of methyltins were very poor.

This Grignard derivatization method had some serious disadvantages, the primary one being that it was not suitable for methyltin species. The method involved a great deal of time per sample, costly instrumentation, and two extractions and a derivatization that significantly reduced recovery efficiency. Its one advantage was that it produced samples suitable for mass spectrometry and thus permitted positive identification of the butyltins.

ANALYSIS OF PIPE FRAGMENT EXTRACTS

Pipe fragment extracts were used to evaluate analytical methods and to determine what compounds were extractable. The pipe samples were analyzed by emission spectroscopy to insure they contained tin, and were roughly ranked according to a semiquantitative estimate of tin content. A PVC and a CPVC sample among the highest in tin content were chosen for testing. A fragmented sample of CPVC #6 was digested in pH 5.7 extractant water for 72 hours at 82 ± 3°C and the resulting water sample was reacted with sodium borohydride. The pH of the extractant water, adjusted by bubbling carbon dioxide through it, varied during initial tests as bubbling rates and times were explored. The 82°C temperature was the maximum reasonable temperature for testing CPVC pipe. Lower temperatures were used in later tests. The extractant water from the CPVC #6 digestion was then extracted with diethyl ether and the concentrated ether extract was analyzed by gas chromatography. The chromatogram, obtained on a 3% (w/w) OV-17 column held at an isothermal temperature of 90°C, revealed six peaks (Figure 9), none of which appeared in the blank. The major peak had the same retention time as dibutyltin dihydride (3.8 minutes). The sample was reanalyzed by gas chromatography/mass spectrometry. No evidence of either tin or chlorine was found in any scan (the two minor, ∿2-minute peaks were not scanned). The chromatographic pattern was similar to one for a similar sample which had not been subjected to the hydride-generation procedure. Electron impact mass spectra (Figures 10 and 11) of the two strongest peaks (3.0 and 3.8 minutes) showed mainly hydrocarbon fragmentation below mass 100. No fragments above mass 100 were present. Methane-chemical ionization mass spectra did not provide much additional information. The isobutane-chemical ionization mass spectrum of the strongest peak (Figure 12) showed a weak ion at a mass-to-charge ratio of 187 which, if attributed to the molecular ion plus 57 mass units, would result in a molecular weight of 130. This was consistent with an octanol isomer and would also account for the small peaks at mass-to-charge ratios of 31 and 45 in the electron impact spectrum.

Octanols could be stabilizer-related compounds resulting from cleavage of the ester bond or from impurities introduced during synthesis. Therefore, octanols were prepared from dibutyltin-bis-isooctylthioglycolate by ester precipitation and saponification according to the scheme of Udris (15). A chromatogram of these alcohols (Figure 13) had two peaks at the same retention times and in the same proportions as in the chromatogram of the extract of fragmented sample CPVC #6. Electron impact mass spectra of the two alcohols (Figures 14 and 15) agreed rather well with the respective CPVC #6 sample spectra (Figures 10 and 11). The specific octanol isomers were not identified because of a lack of reference spectra and reference compounds.

The Grignard derivatization procedure was also used to test water extracts of PVC and CPVC pipe fragments. The extractant water samples, including extractant water rinses of the plastic fragments and the incubation bottle, were extracted twice with a total of 50 mL benzene containing 0.05% (w/v) tropolone (no hydrobromic acid was used in these extractions) and derivatized. Gas chromatographic analyses of the resulting derivatives were performed on a 3% (w/w) OV-17 column, held at 70°C for 4 minutes, then heated

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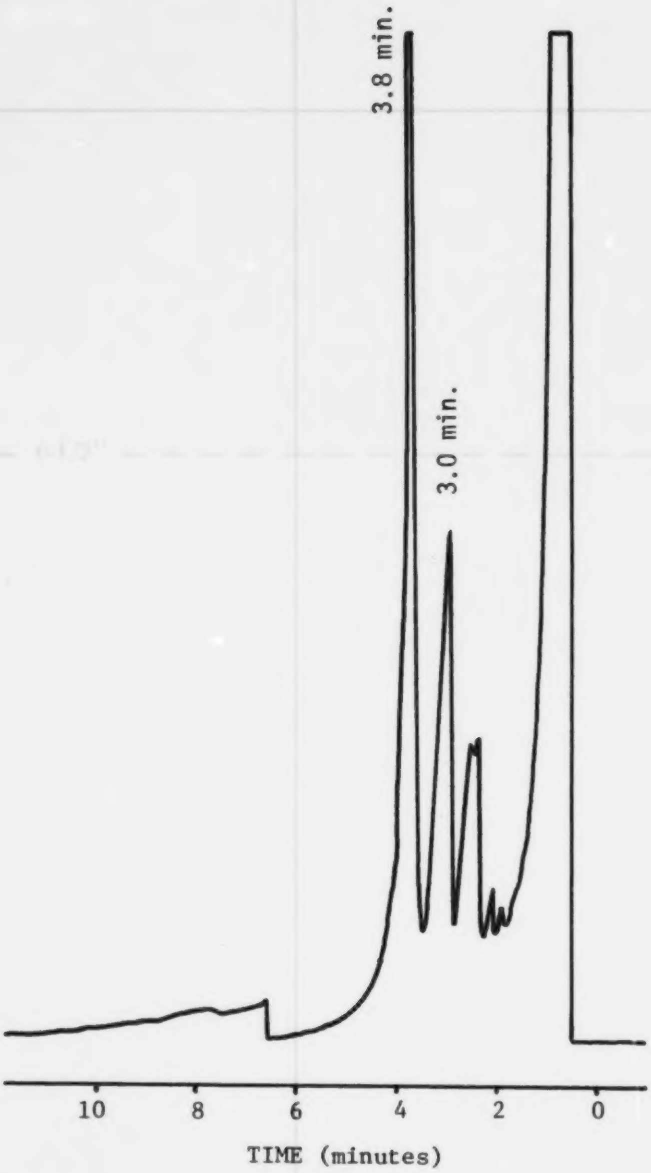

Figure 9. Chromatogram of compounds leached from CPVC #6, on 3% (w/w) OV-17, 90°C isothermal temperature.

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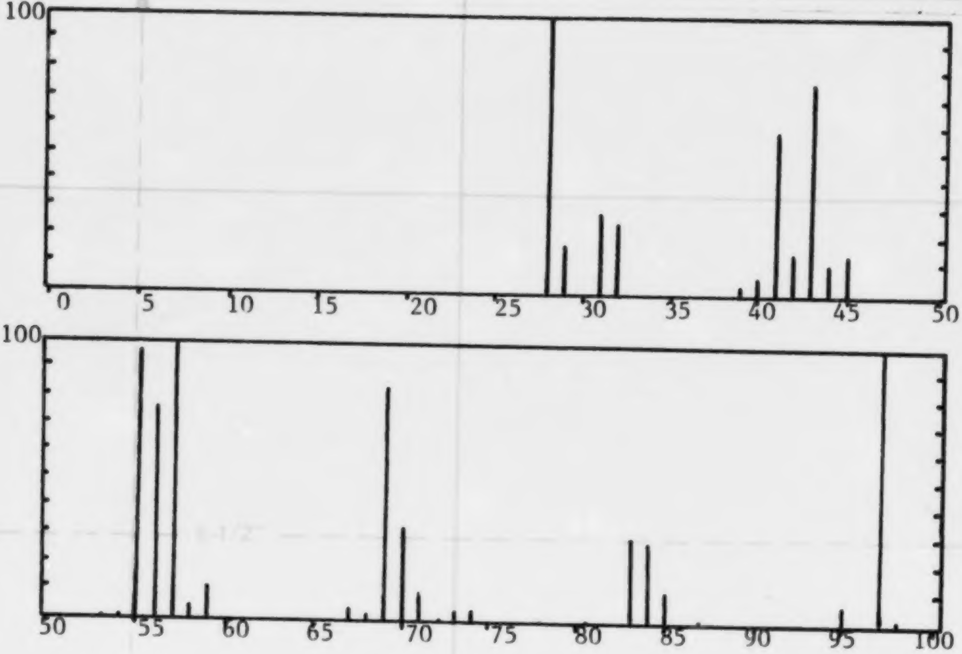

Figure 10. Mass spectrum of the 3.0-minute peak in the chromatogram of CPVC #6.

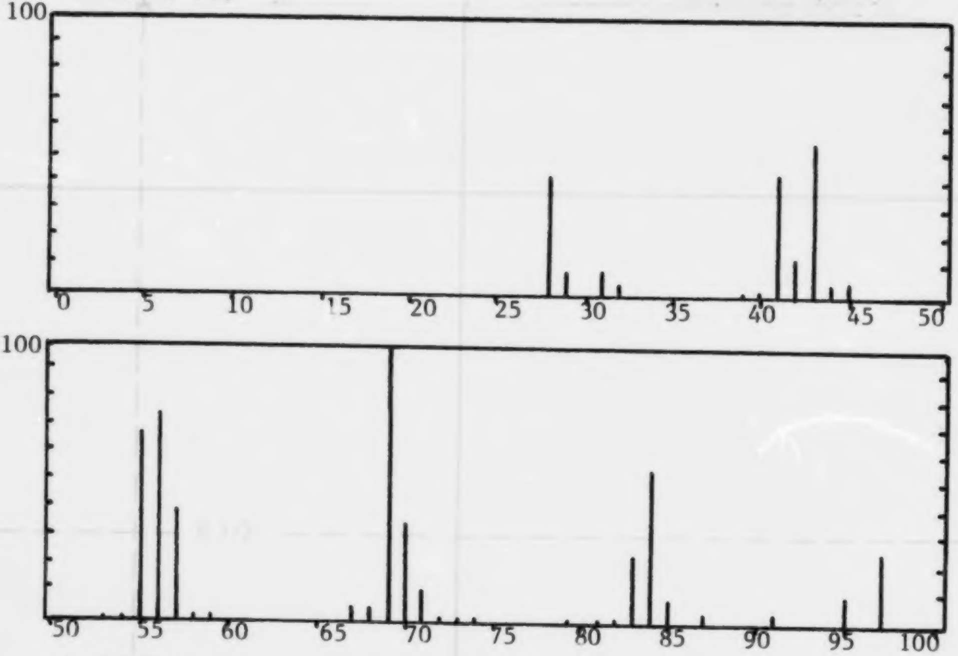

Figure 11. Mass spectrum of the 3.8-minute peak in the chromatogram of CPVC #6.

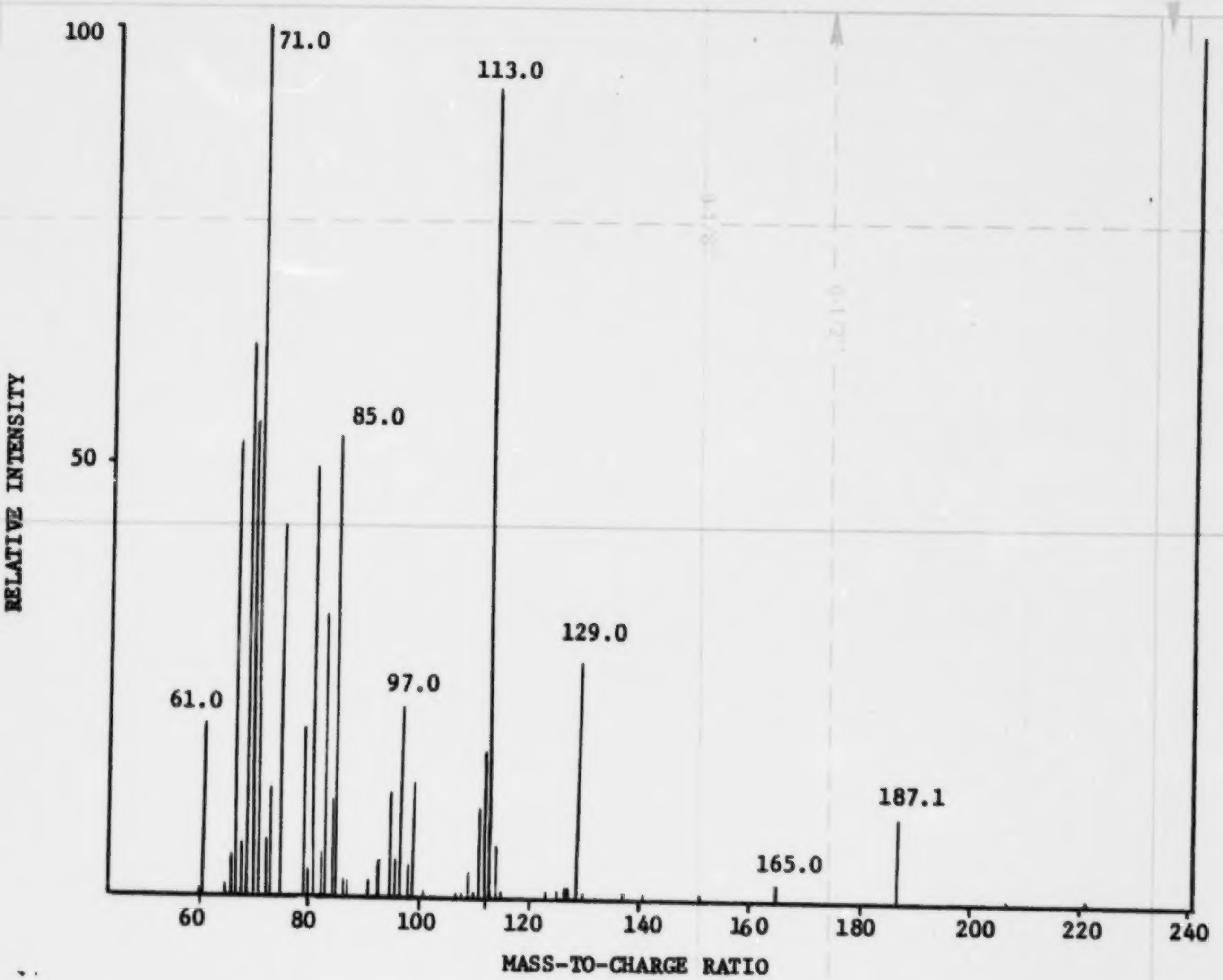

Figure 12. Isobutane chemical ionization mass spectrum of CPVC #6 3.8-minute peak.

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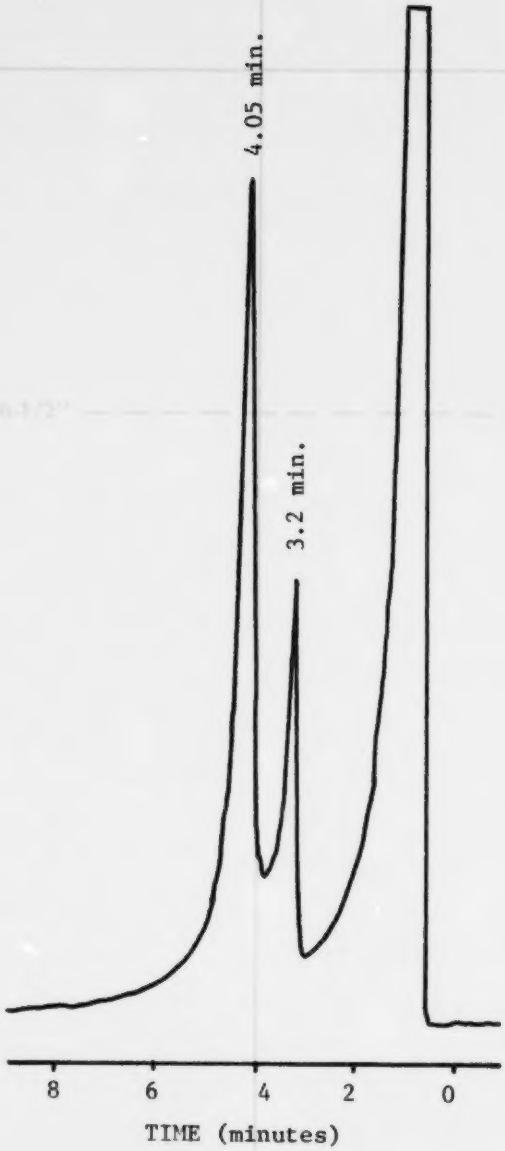

Figure 13. Chromatogram of dibutyltin-bis-isooctylthioglycolate ester saponification products, on 3% (w/w) OV-17, 90°C isothermal temperature.

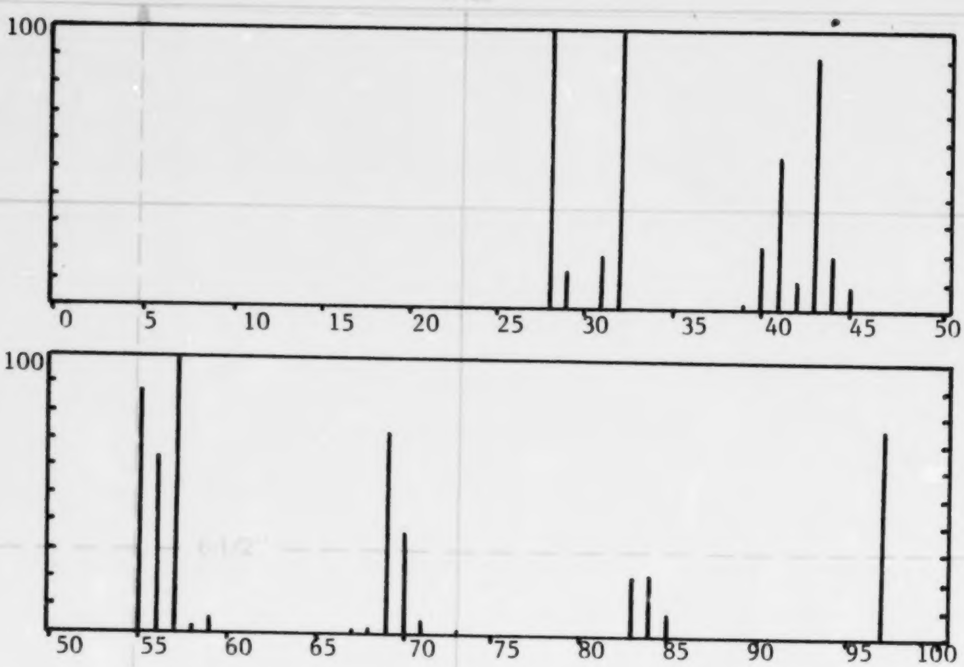

Figure 14. Mass spectrum of the 3.2-minute peak in Figure 13.

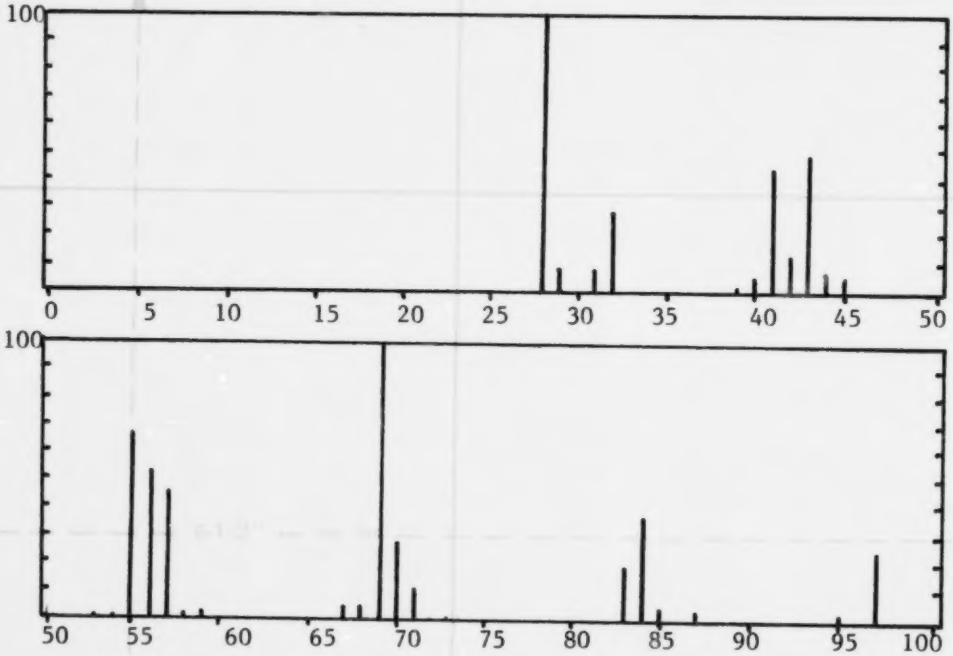

Figure 15. Mass spectrum of the 4.1-minute peak in Figure 13.

at 16°/minute to 240°C. Analyses were also carried out by gas chromatography/mass spectrometry under the same chromatographic conditions. At the approximate retention time of each of the butylmethyltin compounds of interest, several 30 second/decade mass spectral scans were taken in the 125-225 atomic mass unit range. The slower scan speed allowed for a longer dwell time at each mass. Scanning an abbreviated mass range allowed all ions of interest to be detected, not just the six usually handled by our multiple ion monitor.

PVC sample #14A was analyzed by this procedure. It had been incubated in pH 4.9 extractant water at 37°C for 72 hours, and at room temperature for 34 days (it had been prepared for another experiment but was not used). The mass spectrometer total ion current chromatogram of the concentrated Grignard butylation products of this sample was recorded (Figure 16). The mass spectrum scanned at a retention time of 7 minutes showed the presence of dibutyldimethyl tin at masses 147, 149, 151, 203, and 205. The mass spectrum scanned at 9.6 minutes revealed the presence of another organotin compound, tributylmethyl tin. Here a doublet at mass 135 was distinguishable. It represented an organotin fragment ion separating from a more intense hydrocarbon fragment ion at the same mass.

A similarly-treated extract of CPVC sample #14C produced the chromatogram shown in Figure 17. This sample had been incubated 72 hours at 82 ± 3°C, and was stored at room temperature for 11 days prior to analysis. The mass spectrum scanned at 11.4 minutes verified the presence of tetrabutyl tin.

Other peaks in the chromatograms also occurred in the blank (Figure 18). This particular blank was treated in the same manner as PVC sample #14A. The source of some of these peaks was traced to impurities in the n-butyl bromide used to prepare the Grignard reagent. Other peaks may be attributable to impurities in the benzene (Baker 'Resi-Analyzed', distilled-in-glass pesticide grade). It had a considerable amount of toluene in it, as well as two smaller unidentified contaminants. In an attempt to obtain a smaller solvent peak for sample #14C and subsequent samples, Burdick and Jackson benzene was tested. This change in benzene source resulted in a reduction of the 11-to-12-minute hydrocarbon peak and toluene, but not in other contaminant peaks. In spite of these undesirable contaminants, organotin peaks could easily be identified by mass spectrometry.

The tetrabutyl tin found in the sample #14C extract could have arisen from a butyltin compound or from butylation of inorganic tin. In order to distinguish between these possibilities, a second portion of the sample #14C extract was methylated. The chromatogram of the methylation products (Figure 19) showed no distinct peaks, but a mass spectrum scanned at 7 minutes definitely revealed dibutyldimethyl tin, indicating that the water extract did contain butyltin compounds.

Quantitative analysis of an extractant water digest of fragmented PVC sample #14A was conducted using the hydride-generation atomic absorption method. Analysis of 0.1 mL of this sample diluted to 100 mL with doubly-distilled water (Figure 20) showed a dimethyltin dihydride peak. The peak height corresponded to 0.24 ppb dimethyltin dichloride in this diluted sample or 0.24 ppm in the original sample. Analysis of 10 mL of the same sample

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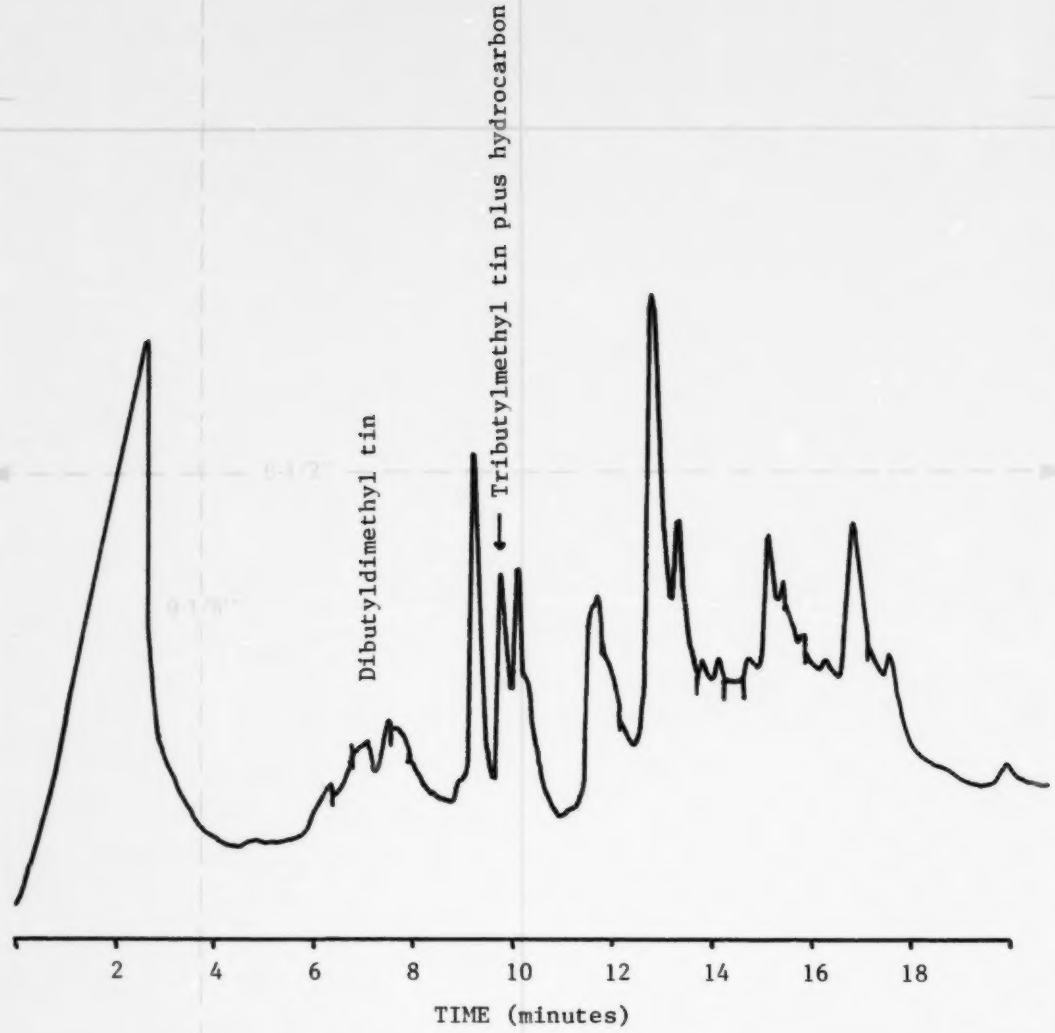

Figure 16. Total ion current chromatogram of the Grignard butylation products of sample #14A.

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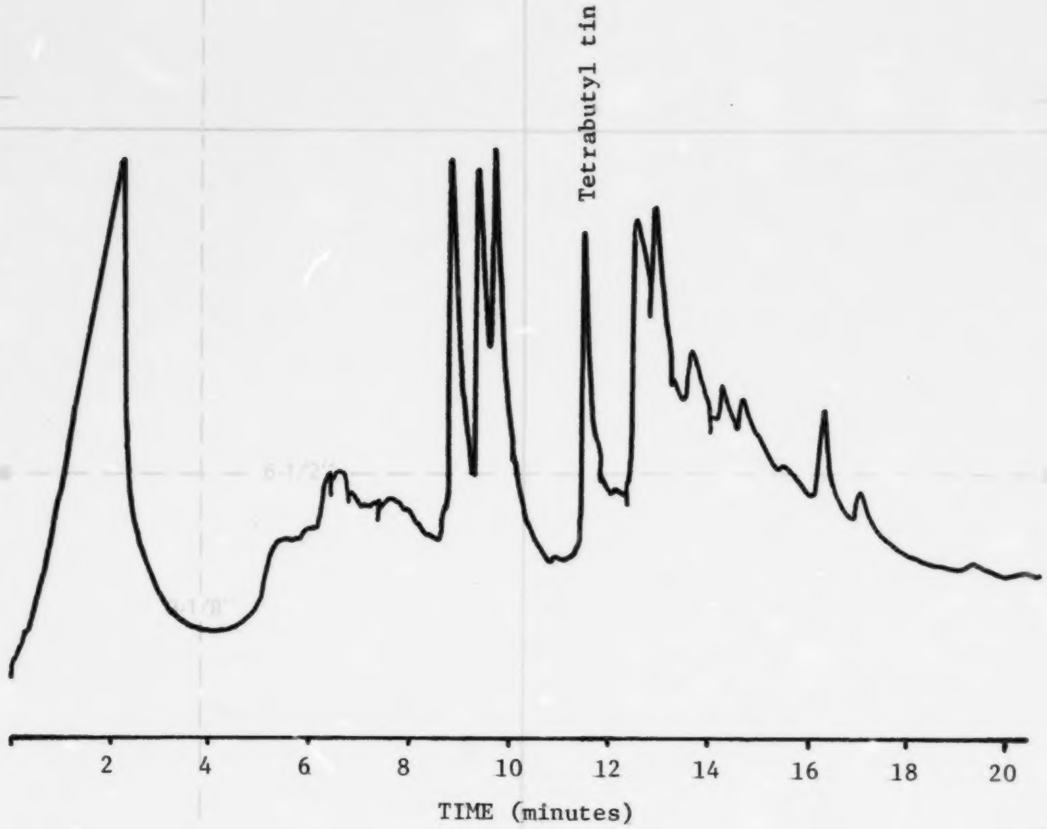

Figure 17. Total ion current chromatogram of Grignard butylation products of sample #14C.

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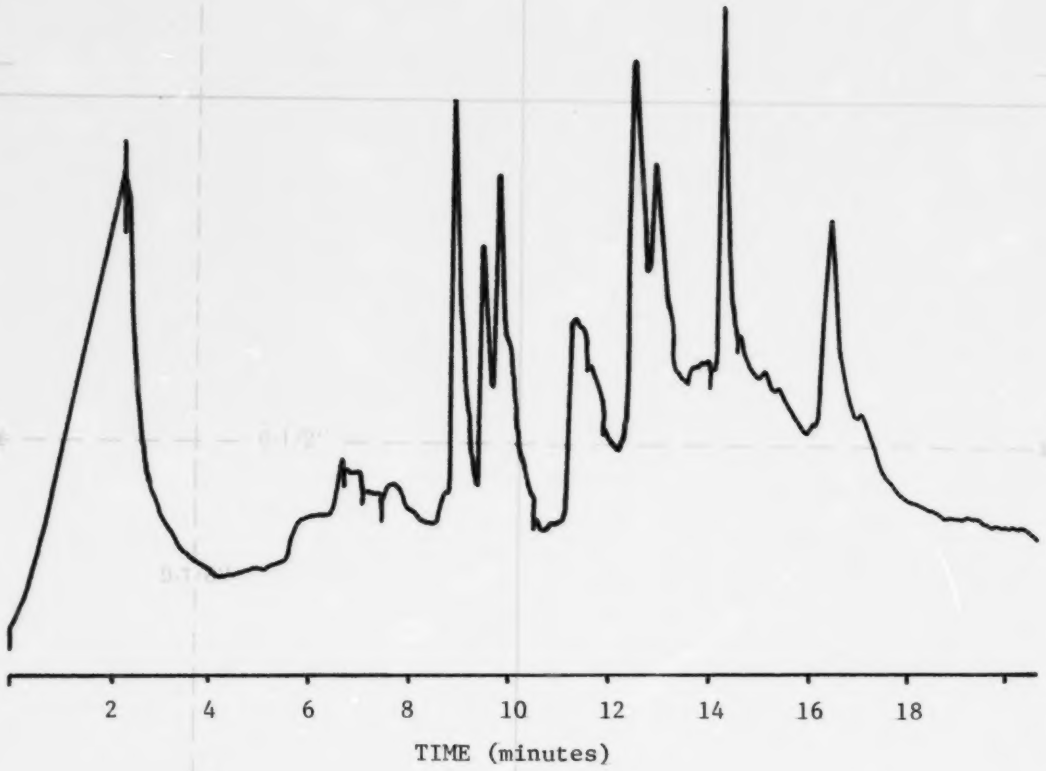

Figure 18. Total ion current chromatogram of Grignard butylation products of blank sample.

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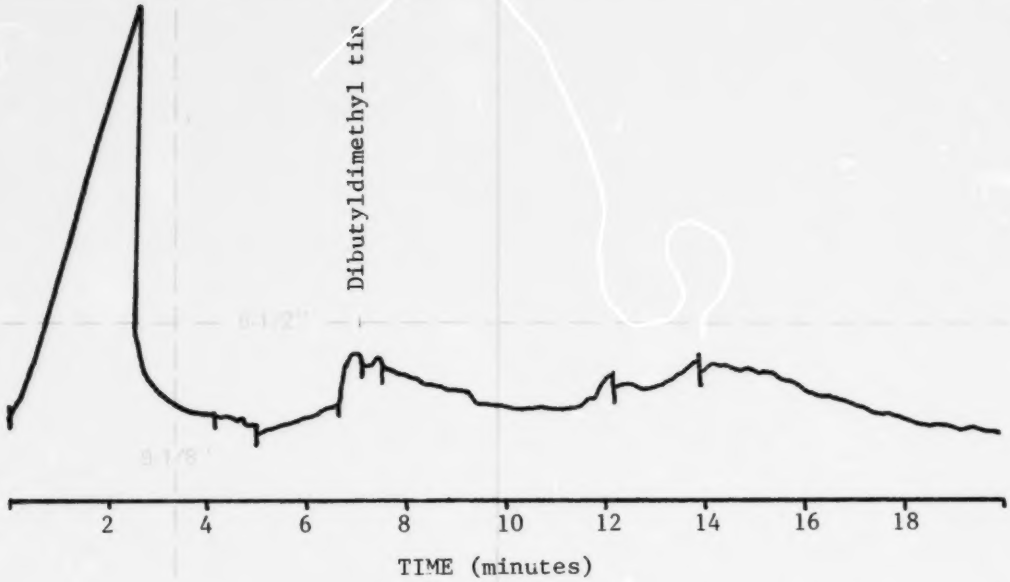

Figure 19. Total ion current chromatogram of Grignard methylation products of sample #14C.

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diluted to 100 mL with doubly-distilled water (Figure 21) showed that all three methyltin species were present in addition to inorganic tin. Quantitation of the small trimethyltin peak presented a problem since it was on the tail of the very large dimethyltin peak. Neither peak height nor peak area could be measured accurately. Our estimate of its concentration was 0.22 ppb in the diluted sample or 2.2 ppb in the original sample. The methyltin peak, well separated from all the other peaks, was not quantitated due to lack of a suitable standard. Inorganic tin was observed in sample #14A blank at about the same level as in sample #14A (∿0.1 ppb).

Both the Grignard and the hydride-generation derivatization methods detected only alkyltin species rather than complete molecules. This meant that an independent analysis had to be set up for the detection and measurement of the isooctyl thioglycolate portion of the stabilizer molecule.

A 100-mL portion of extractant water digest of fragmented PVC sample #14A digested in extractant water at 37°C for 72 hours and subsequently stored at room temperature for a lengthy period, and a 100-mL portion of standard extractant water blank similarly treated, were individually extracted with pentane (Burdick and Jackson). Each pentane extract was concentrated to 1.0 mL and analyzed by gas chromatography, using a 3-foot, 4-mm internal diameter column packed with 10% (w/w) OV-1 and held at an isothermal temperature of 160°C. No evidence of isooctyl thioglycolate or interfering peaks were observed in the sample or blank. Isooctyl thioglycolate, like other isooctyl compounds, gave two chromatographic peaks, as shown in Figure 22.

A calibration curve of isooctyl thioglycolate in pentane yielded a gas chromatographic detection limit of 0.0012 µL/mL or 6 ng injected onto the column when a flame ionization detector was used. Thus 1.2 ppb isooctyl thioglycolate (combined isomers) could be detected after extraction of a one-liter portion of water with pentane and concentration to 1 mL.

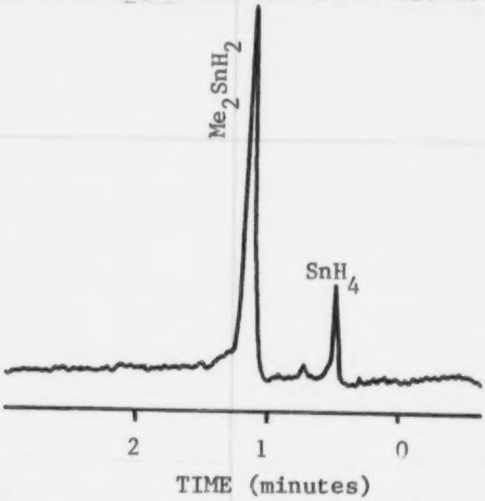

Figure 20. Analysis of extractant water digest of PVC sample #14A by hydride-generation atomic absorption (0.1 mL sample in 100 mL). Me is methyl.

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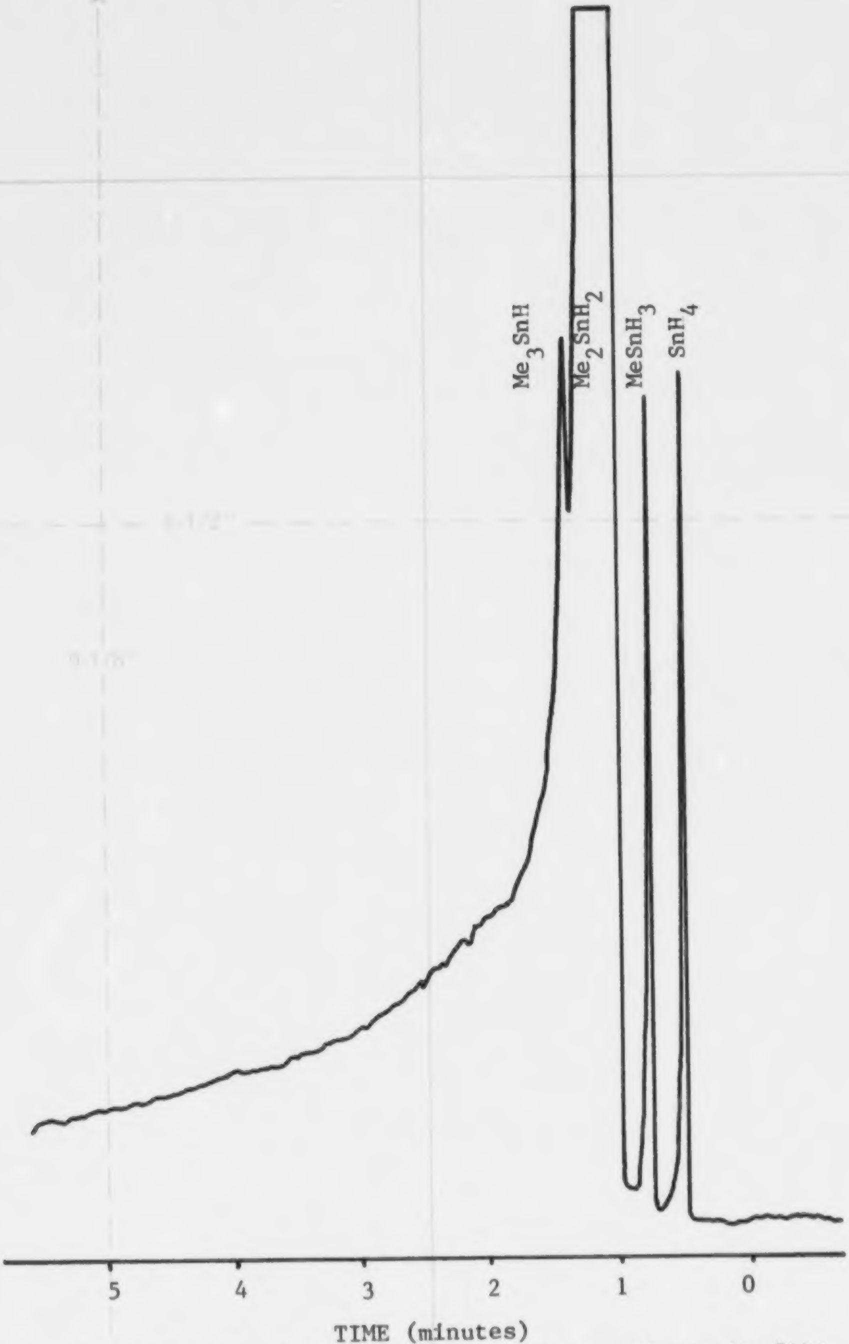

Figure 21. Analysis of extractant water digest of PVC sample #14A by hydride-generation atomic absorption (10 mL sample in 100 mL). Me is methyl.

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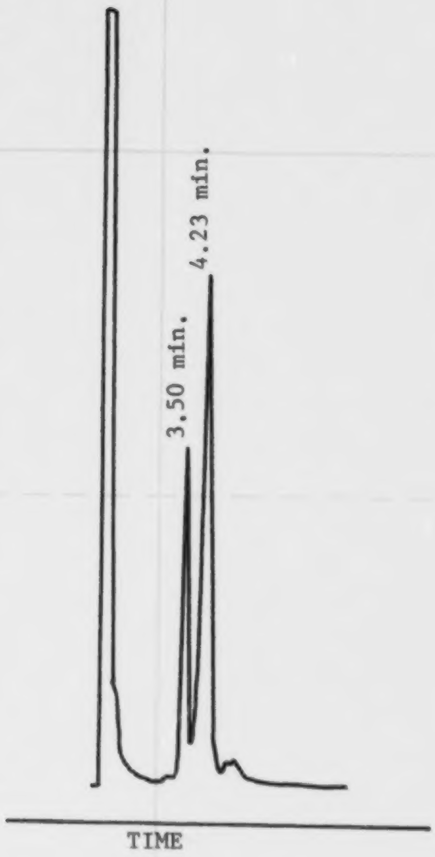

Figure 22. Gas chromatogram of isooctyl thioglycolate on 10% (w/w) OV-1, 160°C isothermal temperature (0.5µL/mL in pentane).

MINIATURE PIPE SYSTEM

During this research program, Wang and Bricker (14) published a paper describing the leaching of organic solvents into water from the cements used in PVC bonding. Consequently, the continuous-flow pipe system described in the Experimental Procedures section was set up for collection of water samples. The analytical procedures used on these samples and the results follow.

Analysis was performed by direct injection of a 5-μL portion of the water sample onto a gas chromatograph column packed with 1% SP-1000 on 60/80 Carbopack B, maintained at an isothermal temperature of 170°C. This was the Supelco column recommended for purge and trap of volatile priority pollutants, and was thus thought to be able to handle significant quantities of water. The analysis was affected somewhat by a variable baseline. When a steep decline occurred during a peak, the sample was injected again. This problem was probably due to a "steam cleaning" effect whereby the superheated water either displaces contaminants from previous samples which had adsorbed onto the column, or displaces a small amount of the column coating. Separation of cement solvents was good, however, as shown in Figure 23. Other columns more tolerant of water were tested. Tenax-GC, when held at 85°C for 2 minutes and then heated at 10°/minute to 230°C, did not separate tetrahydrofuran and methyl ethyl ketone. Porapak P, held at an isothermal temperature of 165°C, retained N,N-dimethylformamide and cyclohexanone longer than was acceptable. N,N-dimethylformamide decomposed under the chromatographic conditions used in obtaining Figure 23.

Standards for tetrahydrofuran, methyl ethyl ketone, and cyclohexanone analysis were prepared by direct injection of known amounts of the solvents dissolved in water. Calibration curves were prepared in the 0-20 ppm range for initial samples and in the 0-10 ppm range for later samples. Standards stored under refrigeration and kept tightly capped gave reproducible results for at least one week, when compared to freshly-prepared standards. Samples of city tap water were collected and quantitatively analyzed from the miniature pipe system for fifteen consecutive days. Flow was adjusted at the faucet to be ~2-4 liters per minute, and the flow during each time span, as well as the cumulative flow through the system, were recorded. Two samples on Day 1 were grab samples taken as water was flowing through the system, just after start-up and after restarting flow after a 4-hour residence time. Other samples were taken by collecting the water in the miniature pipe system after various residence times, before flow was restarted.

Results are summarized in Table 2. Cyclohexanone was only detectable at the 1-2 ppm level in Day 1 samples. N,N,-dimethylformamide was not analyzed. The only samples in which ppm-quantities of solvents were detected in a flowing system were taken on Day 1. After water flowed through the system overnight, the gate valve was closed on Day 2. After two hours a sample was collected, and flow through the system was reestablished for 2 hours. Another sample was then taken and the pattern repeated. On subsequent days, one sample was taken after a 6-9 hour residence time in the system. Flow was maintained at all other times. Part-per-million quantities of cement solvents were detectable for eleven days. During this time, a leak appeared at the gate valve and became progressively worse. On Day 13, the rate of leakage

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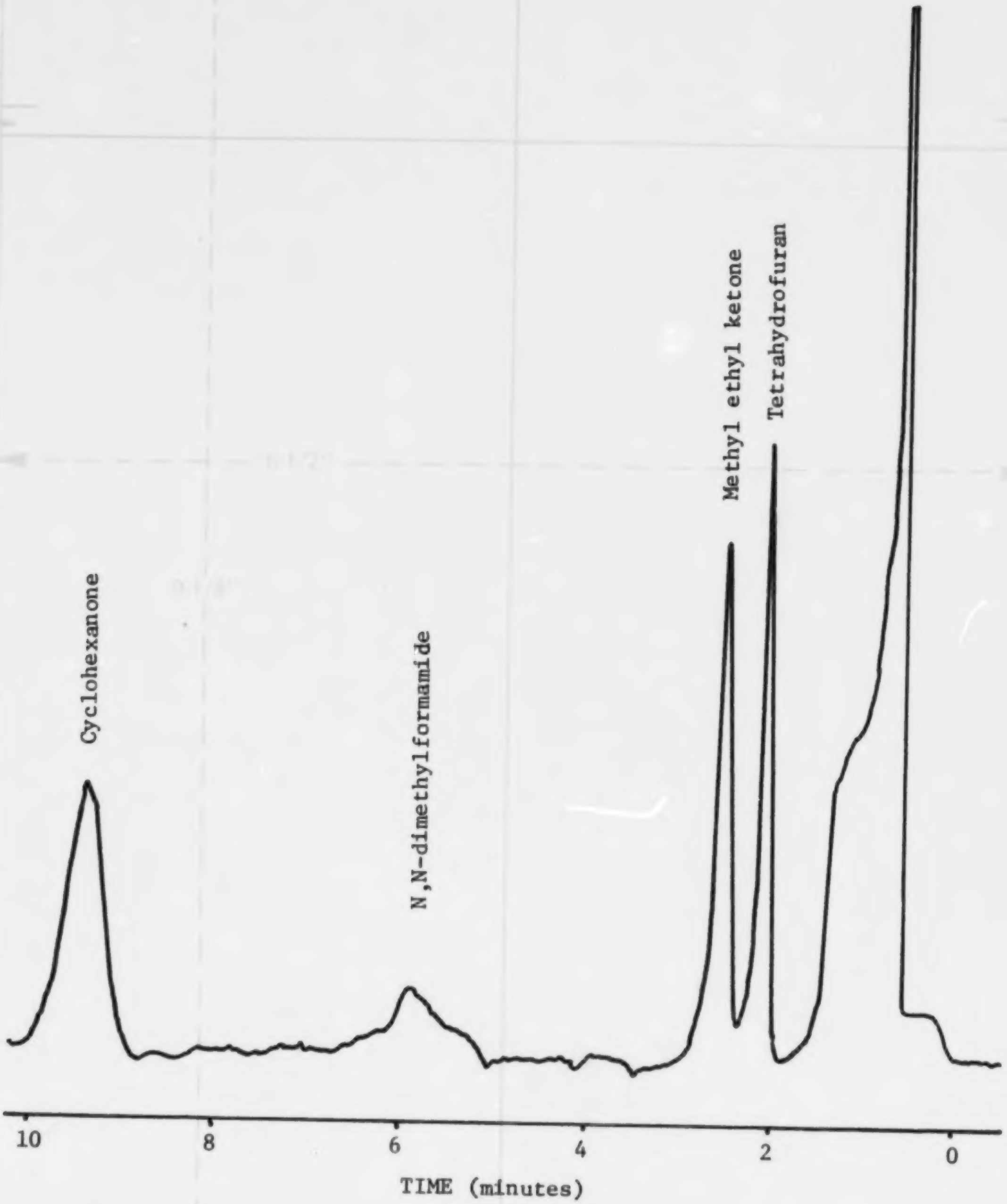

Figure 23. Gas chromatogram of aqueous cement solvent standard on a column of 1% SP-1000 on 60/80 Carbopack B at 170°C.

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TABLE 2. ANALYSIS OF WATER SAMPLES EXPOSED TO CEMENT SOLVENT IN A MINIATURE PIPE SYSTEM

Day	Time Span	Flow Status, cc/min	Approx. Total Flow During Time Span, Liters	Approximate Cumulative Flow Liters	Approximate Cumulative Flow Gallons	THF* ppm	MEK# ppm	MeSn^{+3} ppb	Me$_2$Sn^{+2} ppb	Me$_3$Sn^{+1} ppb
1	3:00p - 3:30p	1875	56	56		19$^+$	23$^+$	-	-	-
	3:30p - 3:45p	off (r)	-	56						
	3:45p - 7:45p	off (s)	-	56	15	8.5$^+$	15$^+$	-	-	-
	7:45p -									
2	10:45a -	1875	1688	1744						
	10:45a - 12:45p	off (s)	-	1744	461	11	17	-	-	-
	12:45p - 2:45p	1875	225	1969						
	2:45p - 4:45p	off (s)	-	1969	520	8	11	-	-	-
	4:45p - 6:45p	1875	225	2194						
	6:45p - 8:45p	off (s)	-	2194	580	6	8	-	-	-
	8:45p -									
3	10:00a	1875	1491	3685						
	10:00a - 4:00p	off (s)	-	3685	973	2.5	4	-	-	-
	4:00p -									
4	10:10a	1875	2044	5729						
	10:10a - 7:10p	off (s)	-	5729	1513	1.5	2.2	-	-	-
	7:10p -									
5	11:15a	1875	1809	7538						
	11:15a - 7:15p	off (s)	-	7538	1991	1.4	2.2	<0.05	0.2	<0.05

(continued)

TABLE 2. (Continued)

Day	Time Span	Flow Status, cc/min	Approx. Total Flow During Time Span, Liters	Approximate Cumulative Flow Liters	Approximate Cumulative Flow Gallons	THF* ppm	MEK# ppm	$MeSn^{+3}$ ppb	Me_2Sn^{+2} ppb	Me_3Sn^{+1} ppb
6	7:15p - 10:00a	4125	3650	11,188						
	10:00a - 6:10p	off (s)	-	11,188	2956	1.1	1.6	0.1	0.4	0.1
7	6:10p - 10:00a	3750	3562	14,750						
	10:00a - 6:00p	off (s)	-	14,750	3897	0.9	1.5	<0.05	0.2	<0.05
8	6:00p - 10:00a	4125	3960	18,710						
	10:00a - 6:30p	off (s)	-	18,710	4943	0.8	1.4	<0.05	0.3	<0.05
9	6:30p - 10:45a	4125	4022	22,732						
	10:45a - 5:45p	off (s)	-	22,732	6006	0.8	1.3	<0.05	0.2	<0.05
10	5:45p - 11:00a	3750	3881	26,613						
	10:00a - 7:00p	off (s)	-	26,613	7031	0.8	1.3	<0.05	0.2	<0.05
11	7:00p - 10:00a	3750	3375	29,988						
	10:00a - 6:15p	off (s)	-	29,988	7923	0.7	1.1	<0.05	0.1	<0.05
12	6:15p - 10:00a	3750	3544	33,532						
	10:00a - 6:30p	off (s)	-	33,532	8859	<0.5	~0.5	<0.05	0.1	<0.05

(continued)

TABLE 2. (Continued)

Day	Time Span	Flow Status, cc/min	Approx. Total Flow During Time Span, Liters	Approximate Cumulative Flow Liters	Approximate Cumulative Flow Gallons	THF* ppm	MEK# ppm	$MeSn^{+3}$ ppb	Me_2Sn^{+2} ppb	Me_3Sn^{+1} ppb
13	6:30p - 10:15a	3750	3544	37,076						
	10:15a - 4:00p	off (s)	-	37,076	9795	<0.5	<0.5	-	-	-
	4:00p - 5:00p	off (r)	-	37,076						
14	5:00p - 2:00p	4125	5198	42,274						
15	2:00p - 10:30a	off (s)	-	42,274	11,169	2.7	5.1	0.1	0.8	0.1

Abbreviations: a = a.m., p = p.m.
(s) = sample
(r) = repair

*Tetrahydrofuran

#2-Butanone (methyl ethyl ketone)

+Samples taken from a flowing system

- Sample not analyzed for organotin species.

was approximately 400 mL per hour. The residence time of water in the miniature pipe system was thus reduced to about one hour, rather than the desired 6-8 hours. After the leak was repaired (without the use of any solvent cement), a considerable amount of water was allowed to flow through the system. A sample was then taken after a long (20.5-hour) residence time. This sample showed solvent values well into the ppm range.

Analysis of a blank, a sample, and appropriate standards for tetrahydrofuran and methyl ethyl ketone took 1-2 hours, while analysis for organotin species took the better part of a day. Therefore, the first few samples were not analyzed for organotin species. When the solvents had not disappeared by Day 5, we felt it was appropriate to test the sample for organotins. All three methyltin species were detectable in all of the samples subsequently analyzed. Their concentrations increased significantly in the Day 15 sample after repair of the leak. It was not determined whether the source of these methyltin species was the solvent cement, the PVC pipe, or the PVC fittings.

A cold water sample was drawn each day from a faucet on the same water line as the miniature pipe system, for use as a blank. Neither solvents nor methyltin species were detected in any blank. The blank did, however, give three later-eluting peaks (Figure 24) by hydride-generation atomic absorption. Since the same pattern was observed at two tin wavelengths, but not while using a hydrogen lamp source, these peaks quite clearly represented organotin species. The major peak corresponded in retention time to either diethyltin, monophenyltin, or monobutyltin species. The source of organotin was unclear. It could have resulted from laboratory contamination of the sample, building plumbing, or the city water supply. Laboratory contamination, always a major concern at part-per-billion levels, was not likely since these peaks showed up consistently in the tap water samples but did not appear in the distilled water blanks. Building plumbing was a possibility, as the faucet from which the blanks were drawn was not often used. There had been some construction in an adjacent area. However, contamination from either our laboratory or the building plumbing should have shown either dimethyltin or dibutyltin species predominating. We are left with the definite possibility that the Ann Arbor water supply may contain organotin species. Several significant storms occurred just before and during the time that these samples were being taken. Agricultural runoff was a possible source, due to ethyltins and/or phenyltins used on fruit crops. Three conclusions were apparent from this experiment. First, ppm quantities of cement solvents and ppb quantities of organotin species were detectable more than two weeks after installation of the system and after over 10,000 gallons of water had flowed through the system. Second, there was no doubt that the substances tested could have been detected longer than two weeks. Third, there was the distinct possibility that our building or municipal water supply contained low-ppb levels of organotin species.

Analysis for these same cement solvents were performed on water samples collected from the pipe loop experiments (next section). However, the results from this miniature pipe system were more meaningful in demonstrating the unexpected persistance of the solvents, inasmuch as the amount of water used in the miniature pipe system was orders of magnitude greater than the amount of water used in a pipe loop.

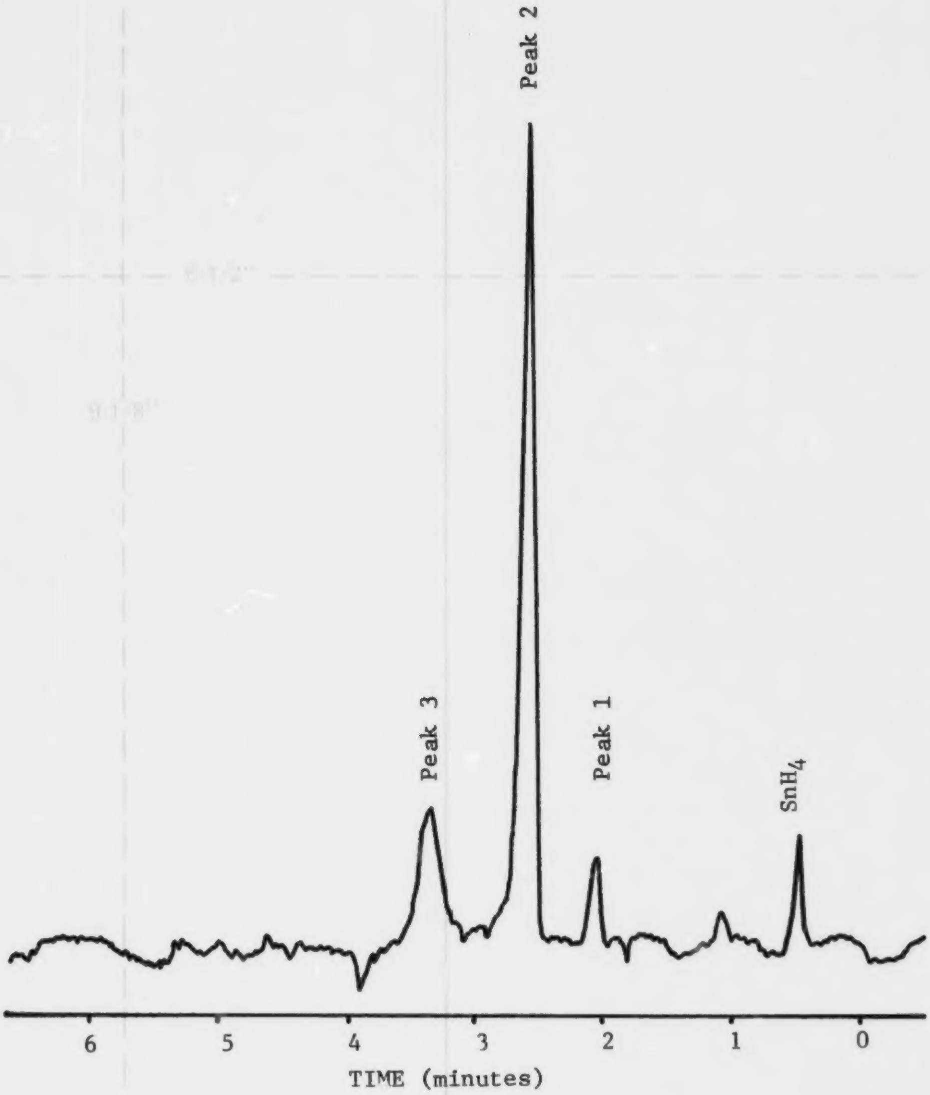

Figure 24. Hydride-generation atomic absorption analysis of tap water blank, showing three unidentified organotin species.

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PIPE LOOP EXPERIMENTS

Two experiments using the continuous-flow closed loop were performed, one with PVC sample #14A and one with CPVC sample #14C. Both experiments were carried out for approximately three weeks, in order to generate data illustrating the rate at which the extracted compounds decreased.

Control Loop

In each experiment a control loop of one-inch internal diameter galvanized pipe, assembled using galvanized fittings, was employed and sampled concurrently to provide blank samples. This 8.9-m (29.2-foot) loop had an inner surface area of approximately 0.71 m^2 (1100 in^2), and required 4.8 L of extractant water to fill. This resulted in approximately one square inch of pipe surface area to 4.4 mL of extractant water. The pH of the extractant water used to fill the loop was 5.0 ± 0.2.

Water samples from the control loop had a slight yellow color due to corrosion of the galvanized pipe. This coloring did not interfere with any analytical procedure.

Only one sample from the control loop had detectable amounts of organotin species. Dimethyltin and trimethyltin species were found in the control loop sample corresponding to the first filling of the CPVC #14C loop. It was assumed that these species arose from laboratory contamination of the batch of extractant water used to fill both the control and sample loops for the first contact period. Therefore, the amounts of dimethyltin and trimethyltin species found in the control loop sample, after correction for a dilution factor, were subtracted from the values obtained from the CPVC #14C sample from the first contact period.

PVC Pipe Loop

The first experiment utilized 8.9 m (29.2 feet) of PVC sample #14A pipe, assembled using solvent-cemented PVC elbows and one metal connector. The stabilizer used in formulating this pipe was dimethyltin-bis-isooctylthioglycolate. This loop had an inner surface area of approximately 0.71 m^2 (1100 in^2), and required 4.1 L of extractant water to fill. This resulted in approximately one square inch of pipe surface area to 3.7 mL of extractant water. The pH of the extractant water used to fill the loop was 5.0 ± 0.2. The PVC sample #14A loop and the galvanized control loop were maintained at 37 ± 1°C.

A total of nine samples were collected from each loop during the exposure period of 21 days and 20 hours. Each loop was filled with extractant water, the water was continuously pumped through the loop for 24- to 96-hour periods, the entire water sample from the loop was drained into a glass carboy, and the loop was refilled with extractant water. Each pump was stopped for about 30 minutes during the draining and refilling process, and the test chamber heaters were off. The test chamber temperature stabilized at the desired value within 30 minutes after resealing. Each draining/refilling process was carried out at the same time of day during the course of the study.

Each sample collected from each loop was analyzed for organotin species and for cement solvents on the day it was collected. Each carboy in which a sample was collected was placed on a magnetic stirrer and stirred with a Teflon-coated stirring bar prior to removal of sample for analysis. A portion of sample for organotin analysis was filtered through Whatman #1 filter paper into a smaller glass container. Successive aliquots of this smaller portion were removed by pipet, after stirring, and placed directly into a hydride generator. An aliquot for cement solvent analysis was removed from the carboy with a glass disposable pipet, placed in a small vial with a minimum of headspace, and sealed with a Teflon-lined cap. An approximately 400-mL filtered portion of each sample was placed in a glass-stoppered reagent bottle, without headspace, and stored at 4°C until completion of the study. The remaining portion of each sample was discarded at the conclusion of analysis on the day it was collected.

Two changes were observed in the extractant water after exposure to the PVC sample #14A pipe loop. First, a yellow color was imparted to all nine water samples. This was apparently attributable to the use of a single, short (1-inch) iron pipe nipple used to join the pipe to the outlet of the pump. At the end of the 22-day study, on dismantling the loop, a small amount of corrosion was noted in this component. Second, the water samples contained small amounts of solid particles, some of which appeared translucent under a low-power microscope. The particles were less than 1-millimeter in length and were present in two physical forms. Some were opaque and irregular, as though fragmented from the pipe, and appeared to match fine, unexposed pipe fragments. Others were translucent flakes or spheres, similar in appearance to flakes of dried solvent cement obtained from around the top of the container. Because this particulate matter affected the reproducibility of repeated runs on each sample, the samples were filtered prior to analysis.

Quantitative alkyltin analyses were carried out using hydride-generation atomic absorption and the method of standard additions. The latter was used to protect against unknown matrix effects brought about by the presence of materials entering the water from the plastic pipe, invalidating any standard curve prepared using distilled water. Because the analyses were carried out in this manner, and because the chlorine interference mentioned earlier was much less for the methyltins, we unknowingly corrected for it. The sample and additions at three levels were generally run in triplicate. This made 12 determinations per sample, and a 12- to 16-hour workday for the analyst, so close duplicates (within 5%) were accepted. There were always three observations at each of two concentration levels, however.

Results of organotin analyses of the nine samples from the PVC sample #14A pipe loop are given, in several different forms, in Table 3. Monomethyltin was only found in the sample from the first contact period, where it gave a peak height of about one twentieth that of the dimethyltin. Results for the dimethyltin and trimethyltin species are expressed in terms of their respective chlorides. The ppb/contact time (1-4 days) is given, along with the concentration in ppb standardized to a 24-hour time period and the

TABLE 3. RESULTS OF ORGANOTIN ANALYSES OF SAMPLES FROM THE PVC SAMPLE #14A PIPE LOOP*

Sample Number	Total Elapsed Time, days	Contact Time of Sample, days	Dimethyltin species, as $(CH_3)_2SnCl_2$ +			Trimethyltin species, as $(CH_3)_3SnCl$ +		
			1	2	3	1	2	3
1	1	1	35. ± 2.0	35.	143.5	13. ± 1.2	13.	53.3
2	3	2	4.8 ± 0.5	2.4	163.2	1.7 ± 0.1	0.85	60.3
3	6	3	1.0 ± 0.2	0.33	167.3	0.21 ± 0.04	0.07	61.2
4	8	2	1.0 ± 0.1	0.50	171.4	0.14 ± 0.01	0.07	61.8
5	10	2	5.6 ± 0.6	2.8	194.4	0.90 ± 0.09	0.45	65.5
6	13	3	3.9 ± 0.6	1.3	210.4	0.75 ± 0.11	0.25	68.6
7	16	3	1.5 ± 0.1	0.50	216.6	0.39 ± 0.01	0.13	70.2
8	20	4	1.0 ± 0.1	0.25	220.7	0.24 ± 0.03	0.06	71.2
9	22	2	0.7 ± 0.1	0.35	223.6	0.10 ± 0.02	0.05	71.6

*The surface area of pipe in contact with extractant water was approximately 1100 in^2. In comparing these results with results of other tests it is imperative to take into account the ratio of exposed pipe surface area to extractant water volume, which in this case was approximately one square inch to 3.7 mL.

+Column 1: Results expressed in terms of ppb/contact time; mean ± standard deviation.
Column 2: Results expressed in terms of ppb/24 hours; mean.
Column 3: Results expressed in terms of cumulative μg leached during the 22-day study; mean.

cumulative amount of each compound, in ug, leached during the course of the test. Statistical information on the precision of the analysis, in terms of the mean and standard deviation, is given in the ppb/contact time column. A total of 223.6 ug dimethyltin dichloride and of 71.6 ug trimethyltin chloride leached into the extractant water during this pipe loop experiment. Subtracting the amounts found for the first contact period, during which high levels would be expected, the totals become 80.1 ug and 18.3 ug for the dimethyltin and trimethyltin chlorides, respectively. All concentrations shown in Table 3 represented significant measurements. The lowest signal-to-noise ratio of any peak quantitated was 4:1, occurring for the trimethyltin chloride in the sample from the ninth contact period.

The results are shown graphically in Figure 25. Here,the increase in leaching during the fifth contact period is very evident. Other results from our work indicated that this increase could be real and consistent. Downes (16) in doctoral work, characterized the migration of total octyltin species from PVC packaging material as a two-phased diffusion process. Desorption of organotin at or near the PVC film surface constituted the initial phase, which was a major contributor to the total migration. The second phase was characterized by internal diffusion through the polymer matrix and into the extracting medium. The migration after surface washing of the PVC film appeared to demonstrate the second phase of the migration pattern.

Results of cement solvent analyses of the nine samples from the PVC sample #14A pipe loop are shown in Figure 26. Cyclohexanone was only detectable in the first five samples (at greater than 1 ppm). Tetrahydrofuran and methyl ethyl ketone were detectable in all nine samples, and were in the 5- to 15-ppm range for the last three samples. This again demonstrated the unexpected persistence of these water-soluble chemicals.

CPVC Pipe Loop

The second experiment utilized 8.9 m (29.2 feet) of CPVC sample #14C pipe, assembled using solvent-cemented CPVC elbows and connectors. The stabilizer used in formulating this pipe was primarily dibutyltin-bis-isooctylthioglycolate. This loop had an inner surface area of approximately 0.71 m^2 (1100 in^2), and required 3.9 L of extractant water to fill. This resulted in approximately one square inch of pipe surface area to 3.5 mL of extractant water. The pH of the extractant water used to fill the loop was 5.0 ± 0.2. The CPVC sample #14C loop and the galvanized control loop were maintained at 72 ± 1.5°C.

A total of seven samples were collected from each loop during the 21-day exposure period. Filling, operating, and sampling these loops were the same as described for the PVC pipe loop. Each sample collected from each loop was analyzed for organotin species and for cement solvents.

In this CPVC pipe loop the iron nipple was replaced with one of CPVC, eliminating the corrosion and sample discoloration problems. However, the plastic particle contamination persisted. The samples were filtered to remove this particulate matter.

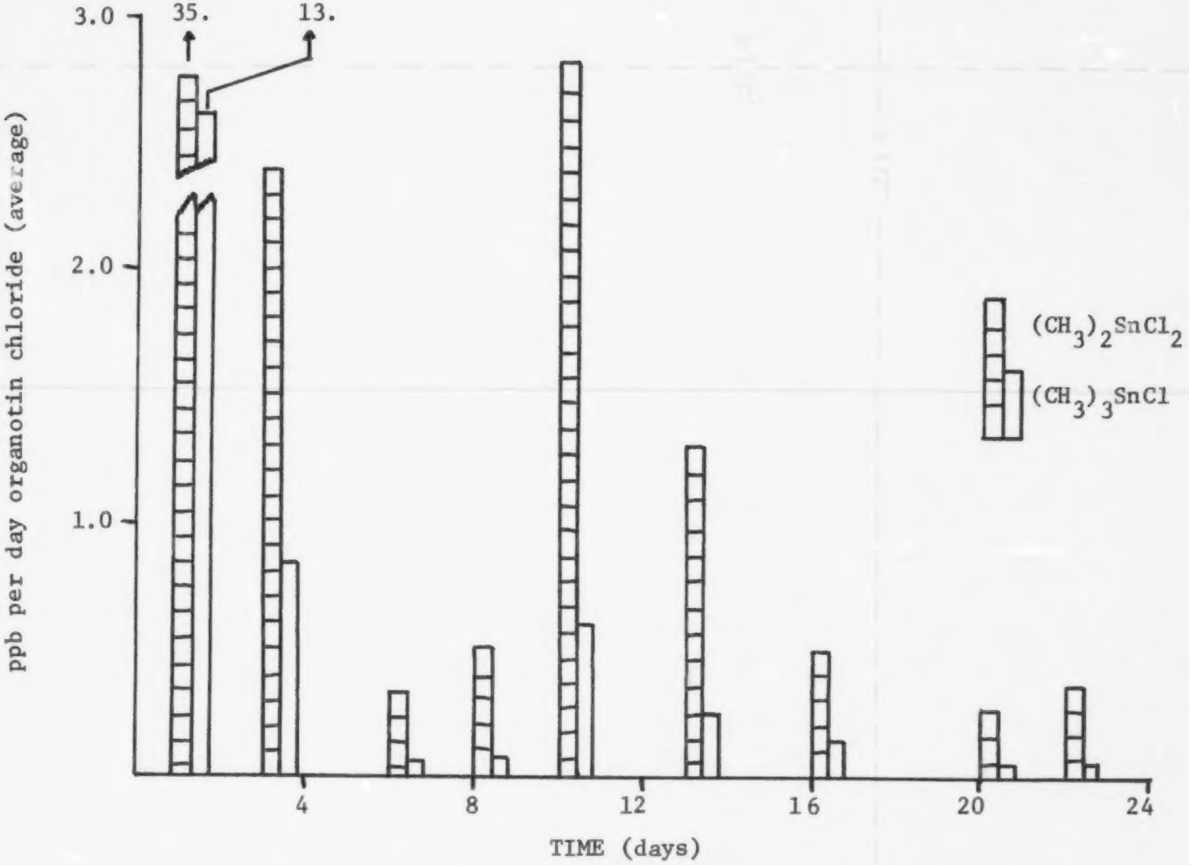

Figure 25. Standardized organotin chloride concentrations observed in PVC sample #14A pipe loop water samples.

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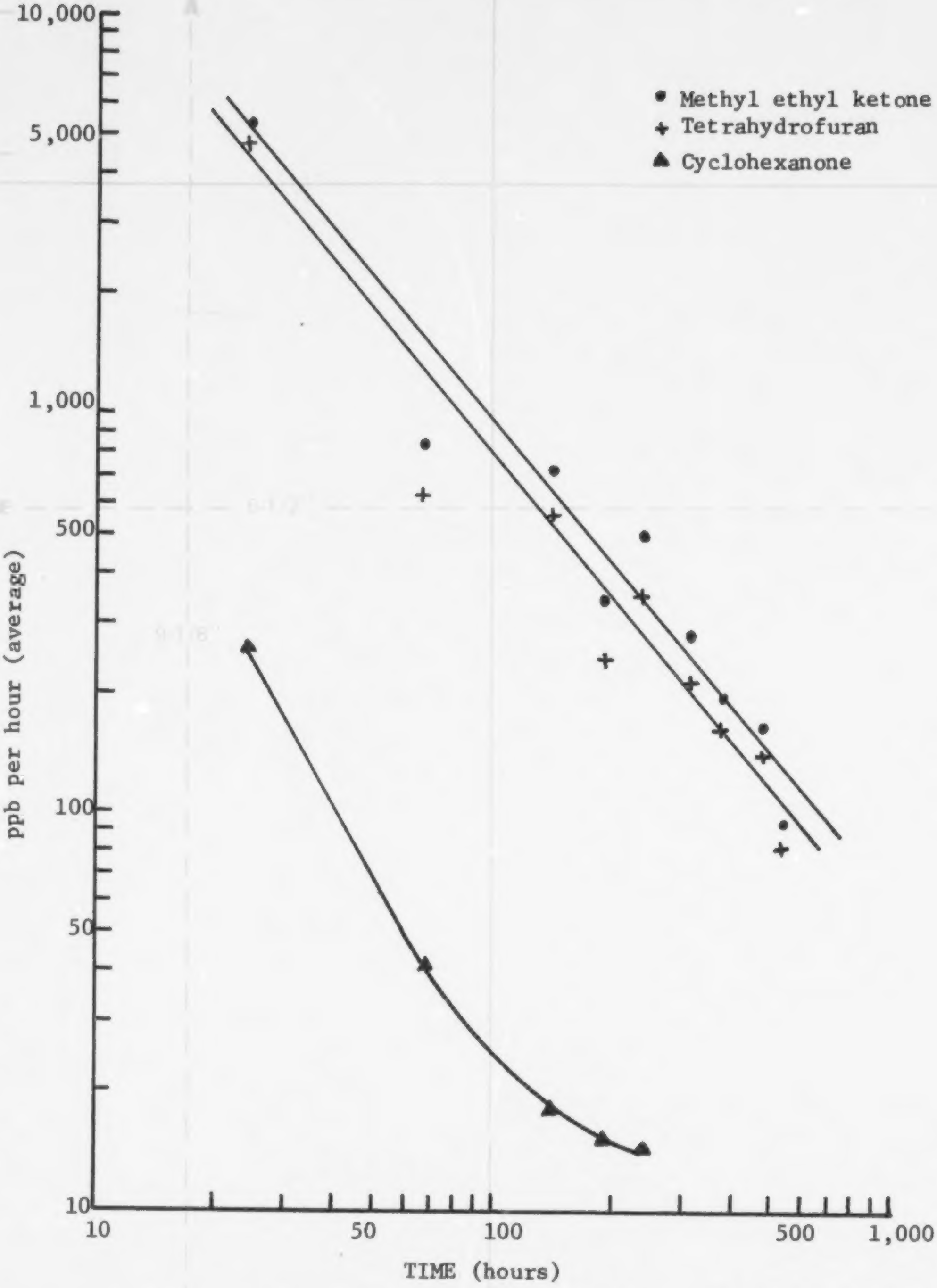

Figure 26. Standardized cement solvent concentrations observed in PVC sample #14A pipe loop water samples.

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It was in the first few analyses of samples from this CPVC loop that the chlorine interference, described in the Hydride Derivatization Method section, was encountered. After tracing the problem samples were dechlorinated, by adding a stoichiometric amount of sodium thiosulfate, as a part of the analytical process. However, this did not solve the interference problem completely, in that it was found that the amounts of alkyltin hydrides formed were not proportional to the amounts of sample used. Time did not permit tracing the source of this problem, so the analytical procedure was changed to work around it. The altered procedure involved running all the samples under the same instrumental conditions, using the same amount of sample for each analysis. Likewise, the same volumes of extractant water containing known amounts of the alkyltin chlorides (dimethyl, trimethyl, monobutyl, and dibutyl) were run as standards. One milliliter of 0.07% (w/v) sodium thiosulfate solution was added to both samples and standards to neutralize the chlorine effect. We might also have used the method of standard additions as used in the PVC loop. However, the standard additions approach would have been more time-consuming, as triplicate determinations of the unspiked sample and each of the three spiked samples would have been required.

The contact period and analytical results are listed in Table 4. Although reported as alkyltin chlorides, some evidence (Appendix A) seemed to indicate that the organotins existed in ionic form in the extractant water. The predominance of the dibutyltin species in the CPVC #14C pipe loop water samples was anticipated as this was the type of organotin stabilizer used in formulating the plastic. A total of 35.7 μg dibutyltin dichloride leached into the extractant water during this pipe loop study, and 25.6 μg of that amount leached into the water after the first contact period. The detected levels of butyltin trichloride in the first four samples were next in magnitude. Dimethyltin dichloride and trimethyltin chloride were also observed in some of the CPVC pipe loop water samples and, in lesser quantity, in the first control loop water sample. The concentrations of these two compounds observed in the first CPVC pipe loop water sample were corrected for the concentrations observed in the control loop water sample. The presence of dimethyltin dichloride persisted in the CPVC pipe loop water through the fifth contact period, but the trimethyltin chloride concentration fell below the detection limit (0.01 ppb/24 hours) after the first contact period. All concentrations reported in Table 4, except the trimethyltin chloride value in the sample from the second contact period, represented significant measurements with signal-to-noise ratios greater than 2:1.

These results are also shown graphically in Figure 27. Again, an increase in some organotin species occurred during the fourth contact period, approximately 10 days into the study.

Water samples from the CPVC sample #14C pipe loop were also analyzed for three of the solvents introduced by the solvent cement. Results (Figure 28) were about the same as in the PVC experiment, although the cements used were slightly different for the two polymers.

PIPE INCUBATION RESULTS

The observations (Figure 29) of the organotin chloride concentrations

TABLE 4. RESULTS OF ORGANOTIN ANALYSES OF SAMPLES FROM THE CPVC #14C PIPE LOOP*

Sample Number	Total Elapsed Time, days	Contact Time of Sample, days	Alkyltin species, as											
			$(CH_3)_2SnCl_2$+			$(CH_3)_3SnCl$+			$C_4H_9SnCl_3$+			$(C_4H_9)_2SnCl_2$+		
			1	2	3	1	2	3	1	2	3	1	2	3
1	1	1	0.61	0.61	2.4	0.30	0.30	1.2	0.63	0.63	2.5	2.6	2.6	10.1
2	3	2	0.34	0.17	3.7	<0.01	<0.01	1.2	0.66	0.33	5.1	2.0	1.0	17.9
3	6	3	0.06	0.02	3.9	-	-		0.39	0.13	6.6	0.84	0.28	21.2
4	10	4	0.12	0.03	4.4	-	-		0.08	0.02	6.9	2.2	0.55	29.8
5	14	4	0.12	0.03	4.9	-	-		-	-		0.80	0.20	32.9
6	17	3	-	-		-	-		-	-		0.60	0.20	35.2
7	21	4	-	-	4.9	-	-	1.2	-	-	6.9	0.12	0.03	35.7

*The surface area of pipe in contact with extractant water was approximately 1100 in^2. In comparing these results with results of other tests it is imperative to take into account the ratio of exposed pipe surface area to extractant water volume, which in this case was approximately one square inch to 3.5 mL.

+Column 1: Results expressed in terms of ppb/contact time.
Column 2: Results expressed in terms of ppb/24 hours.
Column 3: Results expressed in terms of cumulative μg leached during the 21-day study.

-Below the detection limit.

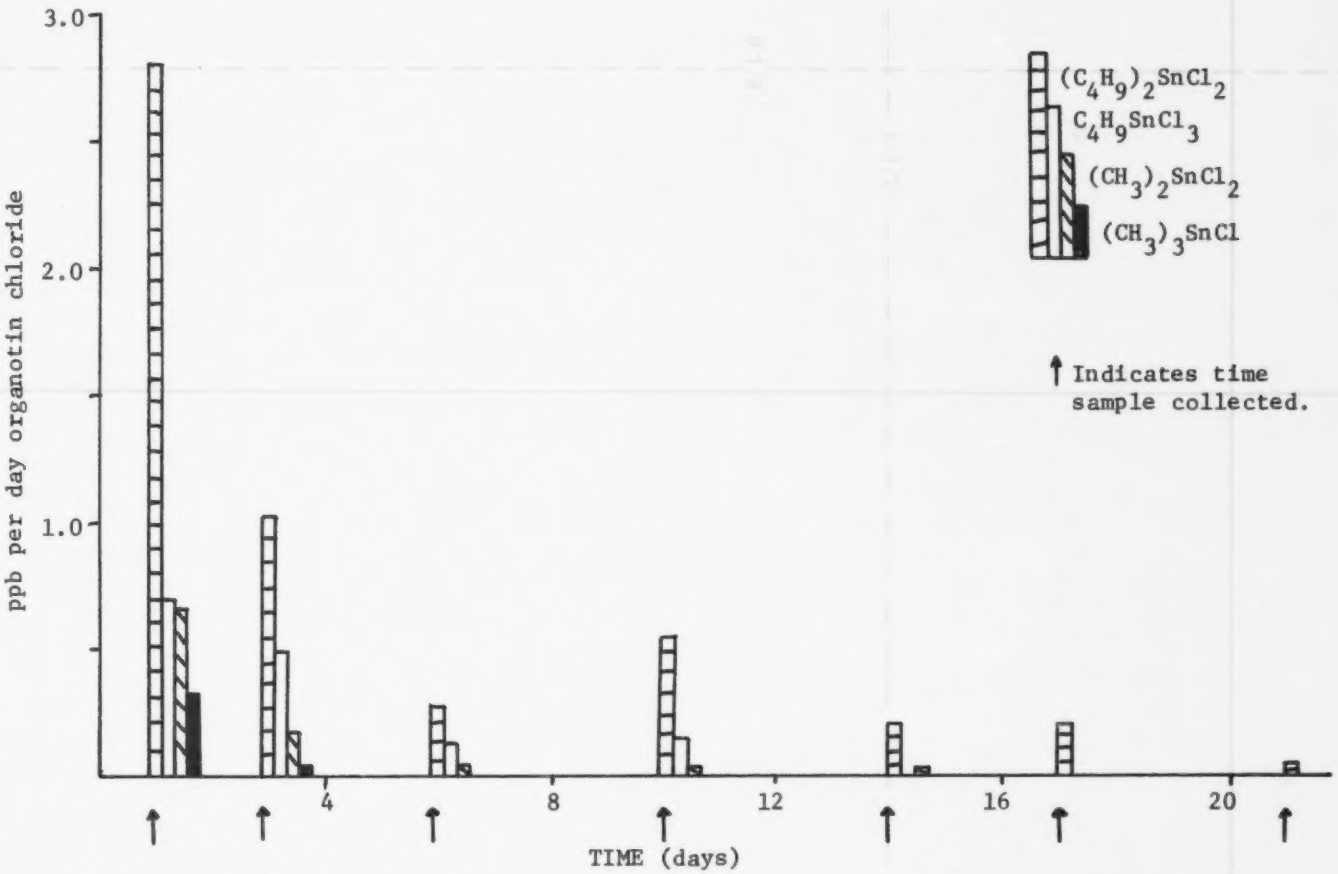

Figure 27. Standardized organotin chloride concentrations observed in CPVC #14C pipe loop water samples.

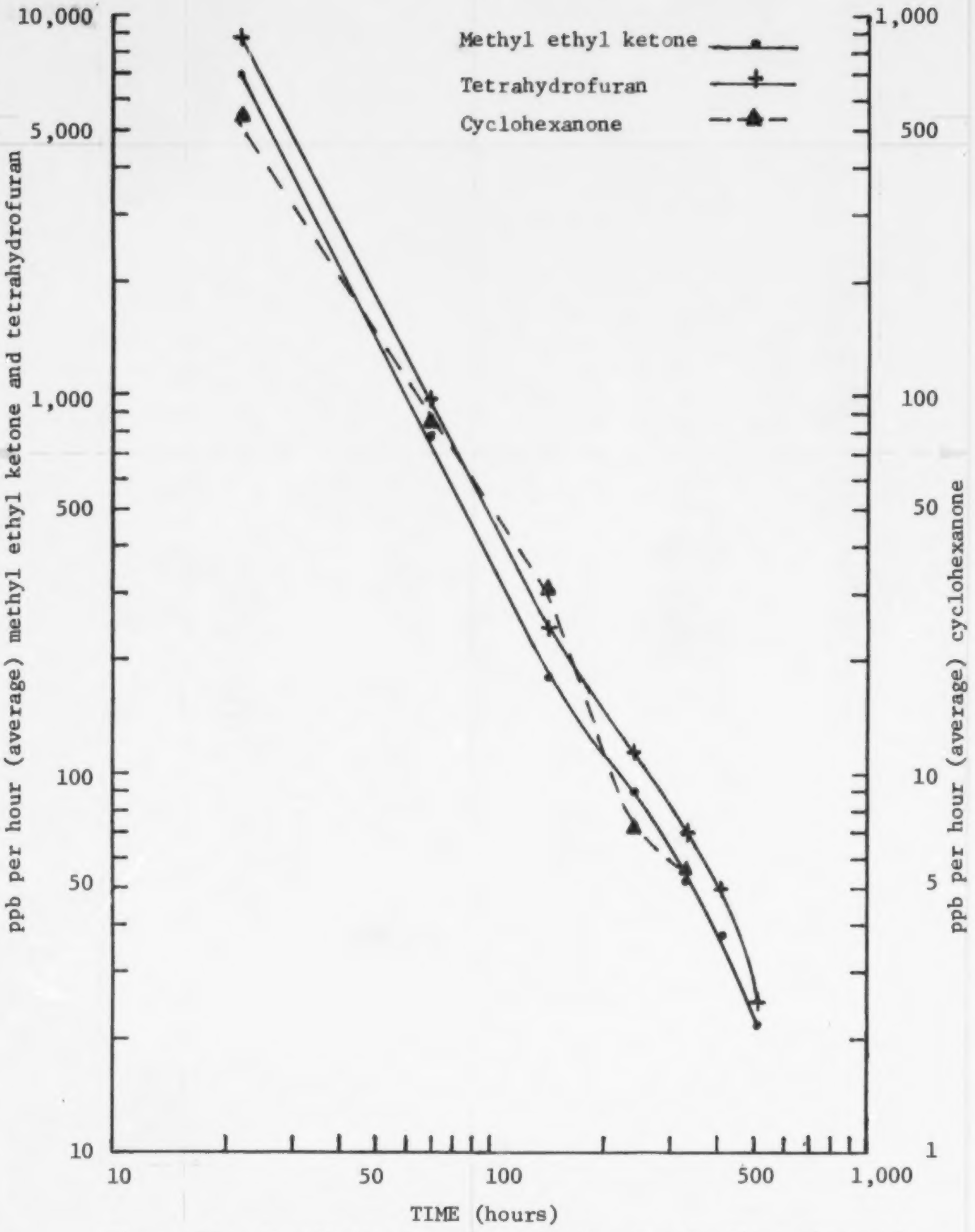

Figure 28. Standardized cement solvent concentrations observed in CPVC sample #14C pipe loop water samples.

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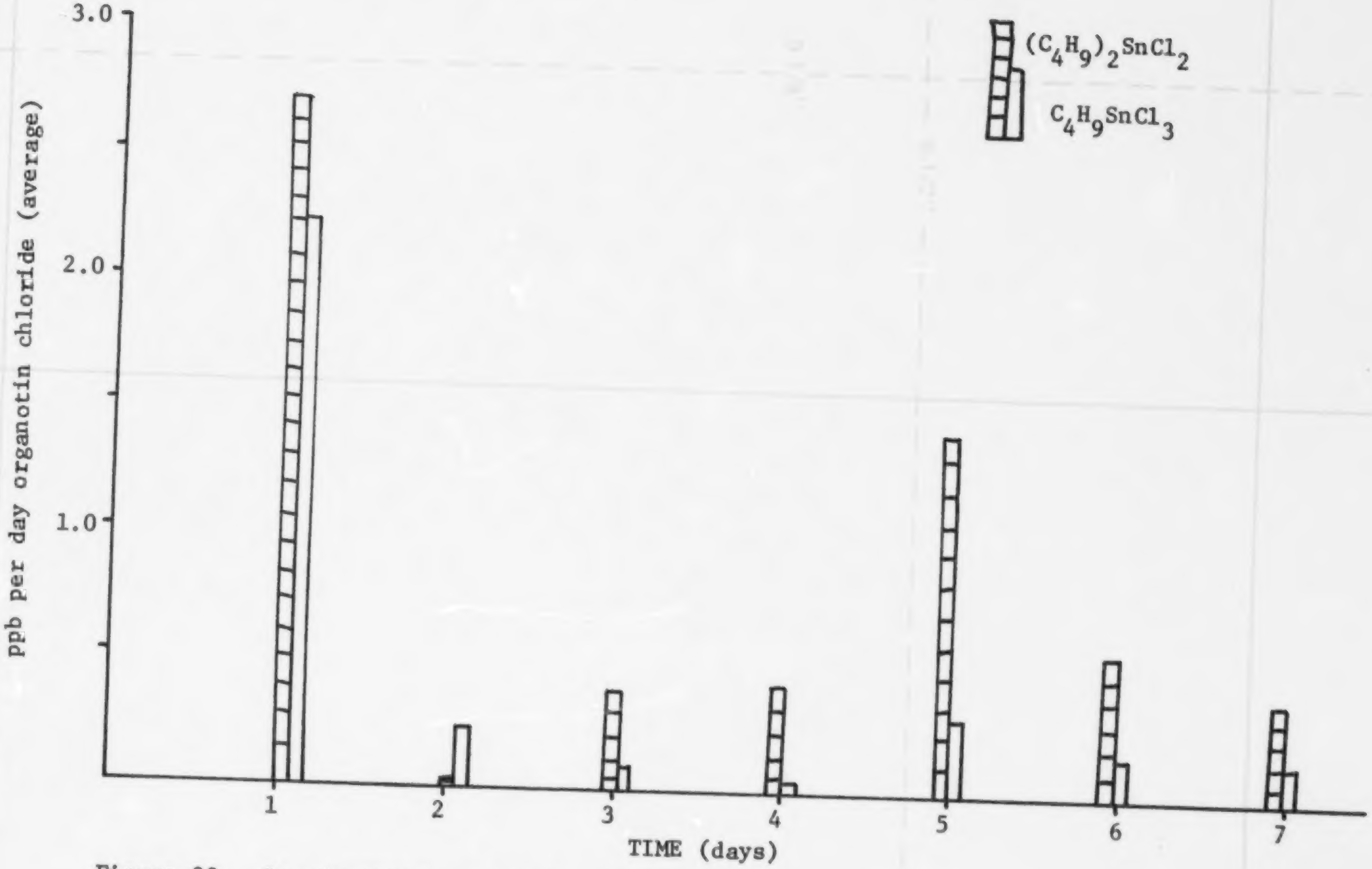

Figure 29. Standardized organotin chloride concentrations observed in CPVC #4 pipe incubation water samples.

in the water samples analyzed in the independent pipe incubation study of CPVC sample #4 were remarkably similar to those in the CPVC sample #14C pipe loop study (Figure 27). A rapid initial decrease in alkyltins was noted, followed by a secondary increase and subsequent decrease. The same species (monobutyl-, dibutyl-, dimethyl-, and trimethyltin) were found, although only the first two were plotted in Figure 29.

Although the exposure conditions differed in the two studies (25°C water temperature and replacement every 24 hours in the CPVC sample #4 pipe incubation study, as compared with 72°C water temperature and replacement every 48-96 hours in the CPVC sample #14C pipe loop evaluation), similar organotin chloride levels were observed. The secondary maximum organotin concentration occurred five days earlier, however, in the pipe incubation study. The reasons for these similarities and differences may be understood more fully after completion of the independent pipe incubation studies.

QUALITY ASSURANCE TESTING

This project was conducted in accordance with EPA Quality Assurance requirements (17). Only class A volumetric glassware was used throughout the study. Absence of organotin contamination in all but one of the many (>100) blank and control samples analyzed attested to the adequacy of the laboratory techniques used and the glassware cleaning procedure, which differed somewhat from standard EPA procedure. Chemicals used for quantitative analysis were reagent grade and were analyzed by appropriate methods to determine their purities.

One aspect of quality assurance preliminary to using the hydride generation method was determining that the responses of the various alkyltin hydrides were reproducible. Four aliquots of a working standard containing the three butyltin chlorides, prepared by serial dilution of an ethanol stock solution, were analyzed successively by the hydride-generation atomic absorption procedure. Retention times and peak heights (Table 5) varied by less than 10%.

Triplicate analyses of samples collected from the PVC sample #14A pipe loop (Table 3) generally varied by about 10%, with occasional excursions up to 20%. It was not possible to determine whether these excursions represented sample inhomogeneity or variability in the analyses.

A quality assurance sample was analyzed along with samples from the PVC sample #14A pipe loop. This sample was prepared in doubly-distilled water and had 3.0 ppb dimethyltin dichloride and 1.4 ppb trimethyltin chloride. The concentrations found by the method of standard additions were 2.9 ppb dimethyltin dichloride and 1.1 ppb trimethyltin chloride. The dimethyltin dichloride result was in good agreement with the prepared concentration, while the trimethyltin chloride result differed from the prepared concentration by about 20%. The larger error for the minor component was not surprising, as its initial response must be kept quite small in order for the response of the major component to remain on scale for the final addition.

One important quality assurance aspect of the hydride-generation method

TABLE 5. REPRODUCIBILITY OF BUTYLTIN HYDRIDE RESPONSES

Compound	Concentration, ppb	Retention Time, minutes	Peak Height, chart divisions Mean ± Standard Deviation
Butyltin trihydride	0.34	3.11-3.23	17.45 ± 1.31 (7%)
Dibutyltin dihydride	0.60	5.38-5.48	48.90 ± 4.54 (9%)
Tributyltin hydride	1.58	6.02-6.09	2.75 ± 4.41 (7%)

could not be addressed in this study, and that was percent recovery. In order to determine percent recovery it was necessary to have either a pure compound which could be introduced into the system in the desired concentration range, or an alternate (and more sensitive) analytical method to determine the amount of alkyltin chloride remaining in the hydride generator at the conclusion of the analysis. A few alkyltin hydrides were commercially available, and others could be synthesized. However, these hydrides were extremely air sensitive, and could not be reliably diluted to the ppb and sub-ppb levels of interest without degradation. Use of permeation tubes for preparation of alkyltin hydride standards has not, to our knowledge, been reported, and was not attempted during this study. Since hydride-generation was the most sensitive method known for analysis of alkyltin species, determination of the amount of alkyltin remaining in the hydride generator after analysis was not possible.

The best method of determining percent recovery for the hydride-generation method would be to use radiolabelled alkyltin species. Scintillation counting of the radioactivity remaining after hydride generation would satisfy the requirement for a more sensitive analytical method. Since these radiolabelled chemicals would have to be custom synthesized, at considerable expense, the recovery study would be more cost-effective if done in conjunction with a low-level toxicity study also requiring radiolabelled chemicals. We have proposed, and remain interested in, both the analytical recovery and toxicological aspects of this problem.

It was possible to show that the hydride-generation responses of alkyltin chlorides in distilled water were reproducible, and that the responses of alkyltin chlorides in the matrix of interest were reproducible and could be made to equal the responses in distilled water by appropriate chemical treatment.

Although the neat alkyltin halides appeared to have limited volatility, there was no evidence that alkyltin halides (or other species) in water would volatilize. Therefore, sample handling was not a problem with the alkyltins.

Quality assurance for the cement solvents was more straightforward (Table 6). Observed concentrations were in excellent agreement with prepared concentrations, as would be expected for the direct analysis procedure used. However, the cement solvents were volatile, and the water drained from the pipe loops was at either 37 or 72°C. Therefore, placing an aliquot of sample in a sealed container was done as quickly as possible. Since Wang and Bricker (14) used purge and trap in analysis of cement solvents, and achieved less than 15% recoveries due to their polar nature, volatility was not thought to introduce any major uncertainty in the results.

TABLE 6. ACCURACY OF OBSERVATIONS OF CEMENT SOLVENTS

Standard	Concentration, ppm		% Recovery
	Theoretical	Observed	
Tetrahydrofuran 1	8.9	8.9 ± 0.5	100 ± 6
Methyl ethyl ketone 1	8.0	8.0 ± 0.5	100 ± 6
Tetrahydrofuran 2	2.2	2.2 ± 0.1	100 ± 5
Methyl ethyl ketone 2	4.0	4.1 ± 0.1	103 ± 2
Tetrahydrofuran 3	89.	99. ± 3	111 ± 3
Methyl ethyl ketone 3	81.	78. ± 5	96 ± 6
Cyclohexanone 1	2.0	2.0 ± 0.05	100 ± 3

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APPENDIX A

Many of the conventional separation, concentration, and detection techniques were investigated as to their applicability to this research. Our experiences with these, mostly negative, are described in this section.

CONCENTRATION, SEPARATION, AND DETECTION OF ORGANOTIN COMPOUNDS

Column concentration and solvent extraction were tested as methods for removing and concentrating various organotin species from water.

Sample Concentration Using XAD-Resin

Several attempts were made to evaluate the applicability of XAD-2 resin to removing and recovering organotin compounds from water standards. In the first experiment a dibutyltin dichloride standard containing 1-ppm Sn was applied to the column which was then washed with distilled water and eluted with acetone. The latter was chosen because it was a good solvent for all but one of the commercial stabilizers on hand. No tin was detected in the sample, wash, or acetone effluents from the XAD-2 column. The procedure was repeated with hexane and benzene as the eluants with the same results. Water standards containing 0.5 or 2% (v/v) of 48% (w/v) hydrobromic acid, the concentrations of acid used in the Meinema (1) liquid-liquid extraction technique, were then applied to the column, and the latter washed with distilled water acidified with the corresponding amount of hydrobromic acid, and eluted with benzene. Most of the tin was recovered in the benzene eluant, but was only semiquantitatively determined by flameless atomic absorption due to matrix effects. The remaining amount of tin was not retained on the resin, but was detected in the sample and wash effluents.

Aqueous standard dibutyltin-bis-laurylmercaptide and dibutyltin-bis-isooctylthioglycolate solutions were prepared from acetone stock solutions, and applied to an XAD-2 column. The latter was washed with distilled water, and eluted with hexane since these standard materials were both relatively nonpolar. No tin was detected in the sample, wash, or solvent effluents. Aqueous standard solutions of the same two compounds were prepared from ethanol stock solutions and applied to an XAD-2 column. After a distilled water wash, the compounds were eluted with 50:50 methanol/water containing 0.5% (v/v) of 48% (w/v) hydrobromic acid. Again, no tin was found in any column effluent. The laurylmercaptide and isooctylthioglycolate aqueous standard solutions were cloudy, with the ethanol stock solution resulting in slightly clearer standards than the acetone stock solution. This indicated some dissociation or reaction had occurred, and also indicated that the two test chemicals may not exist in compound form in aqueous solution.

It appeared that acid was necessary for the successful removal of tin compounds from the XAD-2 resin, most likely due to ionization of organotin compounds in acetone and/or water. This corresponded with the work of others which showed acid was necessary in thin-layer chromatography, high-pressure liquid chromatography, extraction, and other analytical procedures. However, the compounds we were attempting to analyze were very reactive and unstable. Addition of acid precluded determining the exact organotin compound or species which existed in water.

Organic Solvent Extraction

Liquid-liquid extractions were carried out on dibutyltin dichloride using several solvents. In these experiments an aqueous solution of dibutyltin dichloride, containing 0.2-ppm Sn, was prepared from a 1000-ppm stock solution, previously prepared with acetone as solvent. Fifty mL of this dilute solution were placed in a separatory funnel, 5 mL of test solvent were added, and the liquid was shaken vigorously for several minutes. The aqueous and organic layers were separated and each analyzed for tin by flameless atomic absorption. The responses of the solvent extracts were compared with those of standards prepared in the respective solvents. The results appeared erratic due to matrix effects and should be considered indicative of trends rather than absolute values. The percentages of tin remaining in the aqueous phase after extraction with various organic solvents are listed in Table A-1.

The best recovery of dibutyltin dichloride from an aqueous solution was obtained when the water was acidified with hydrobromic acid (to 2% v/v acid) and then extracted with benzene according to the procedure of Meinema. The 80% recovery of Sn agreed well with the results of Meinema. To establish the composition of the recovered tin compounds, the following experiments were performed.

Dibutyltin Dichloride Extraction--

Two 250-mL test solutions of dibutyltin dichloride containing approximately 2-ppm Sn, were prepared in water containing 2% (v/v) of 48% (w/v) hydrobromic acid from a 1000-ppm Sn stock solution which was previously prepared with acetone as a solvent. Each of these test solutions and a 250-mL acidified water blank were extracted with 12.5 mL benzene. The benzene extracts were concentrated and analyzed by gas chromatography. The acetone stock solution, which had previously yielded a mass spectrum consistent with dibutyltin dichloride, gave a GC peak with a retention time of 4.4 minutes after two priming injections. The concentrated extracts of the two test solutions did not show 4.4-minute peaks. Instead, they each showed a sharp, 6.7-minute peak superimposed on a broader peak appearing at 6.1 - 6.9 minutes. A number of mass spectral scans indicated that the broad peak represented the mixed-halide compound dibutyltin bromide chloride with some dibutyltin dichloride on its leading edge, and the sharp peak represented dibutyltin dibromide. Figure A-1, a mass spectrum of the sharp 6.7-minute GC peak, showed the mixture of dibutyltin bromide chloride and dibutyltin dibromide. Neither compound showed a molecular ion, but both showed peaks due to loss of one butyl group. The butyl ion at mass 57 was the most intense in the spectrum. Note that intensities of ions above mass 75 were multiplied by a factor of 10.

TABLE A-1. EFFICIENCY OF SOLVENT EXTRACTION OF DIBUTYLTIN DICHLORIDE FROM WATER

Solvent	% Tin Remaining in Aqueous Phase
Hexane	64
Diethyl ether*	92
Methylene chloride	36
1,1,1-Trichloroethane	32
Carbon tetrachloride	68
Trichloroethylene	61
Tetrachloroethylene	112
Benzene, from 0.5% Hydrobromic acid[+]	66
Benzene, from 2.0% Hydrobromic acid[+]	20

*10 mL solvent used due to water solubility.

[+] Water standard acidified with Hydrobromic acid prior to extraction.

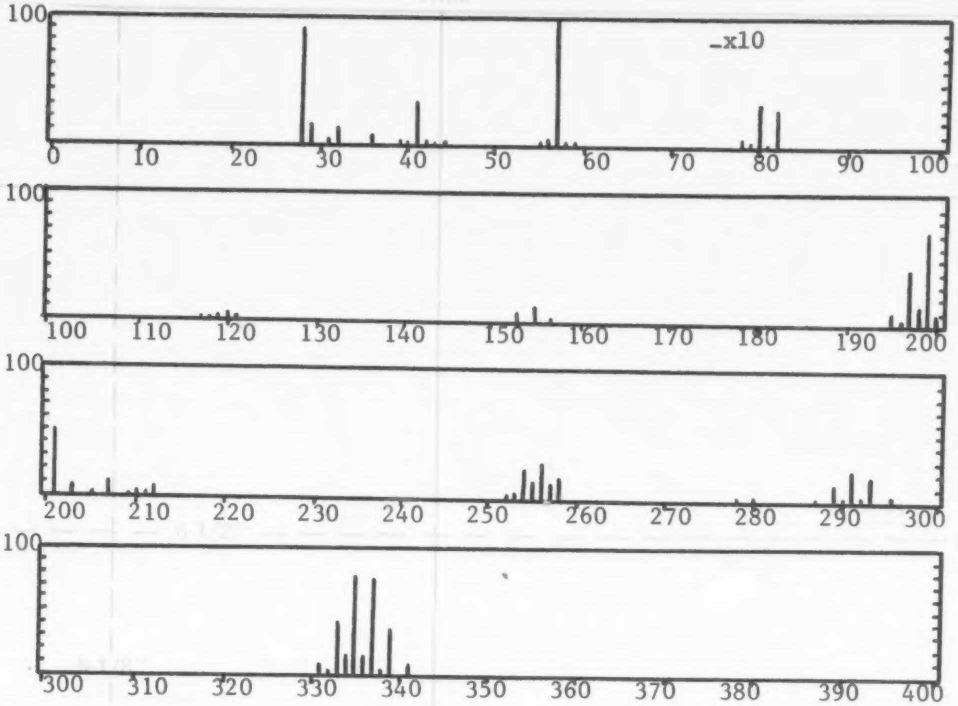

Figure A-1. Mass spectrum of dibutyltin bromide chloride and dibutyltin dibromide from hydrobromic acid/benzene extraction of a dibutyltin dichloride water standard.

Explanation: Calculated versus observed isotope abundances are included to aid in determining the quality of the spectrum.

Mass	Compound	Assignment	Relative Abundance Calculated	Relative Abundance Observed
287	Bu_2 Sn Br Cl	M^+-57	0.21	0.04
289	Bu_2 Sn Br Cl	M^+-57	0.62	0.57
291	Bu_2 Sn Br Cl	M^+-57	1.0	1.0
293	Bu_2 Sn Br Cl	M^+-57	0.73	0.74
295	Bu_2 Sn Br Cl	M^+-57	0.15	0.13
331	Bu_2 Sn Br_2	M^+-57	0.15	0.10
333	Bu_2 Sn Br_2	M^+-57	0.56	0.53
335	Bu_2 Sn Br_2	M^+-57	1.0	1.0
337	Bu_2 Sn Br_2	M^+-57	0.93	0.95
339	Bu_2 Sn Br_2	M^+-57	0.34	0.44
341	Bu_2Sn Br_2	M^+-57	0.05	0.08

There were several possible explanations for this result. First, it was well known that a simple halogen exchange occurred with organotin halides. This was certainly a contributing factor but did not explain why the hydrobromic acid was so critical to obtaining good extraction efficiency. Dibutyltin dichloride was at least 100 times more soluble in most organic solvents than in water at room temperature. On that basis alone, a favorable partitioning from water into an organic phase should have occurred. Obviously, there were overriding factors preventing this.

The second possible reason may be that dibutyltin dichloride dissociated in water, and in the presence of a large excess of hydrobromic acid, was driven back into the organic-extractable halide form. Dimethyltin dichloride was almost completely dissociated in water with some hydrolysis occurring to produce an acid solution (2). Conductivity measurements of methyltin and ethyltin halides have shown them to be good conductors when dissolved in methyl alcohol, ethyl alcohol, water, acetone, or pyridine, and poor conductors when dissolved in benzene, ether, nitrobenzene, or nitromethane (3). During the study we observed that benzene solutions of dibutyltin dichloride produced about twice the gas chromatographic response of solutions of the same concentration prepared in acetone or ethanol. Perhaps non-chromatographable ionic species were being formed in the two polar solvents. The degree of dissociation of dibutyltin dichloride in water will determine its exact organotin speciation in this solvent, but dissociation data for this compound were not located in the literature.

Reaction of dibutyltin dichloride with water was another possible explanation. Dialkyltin dihalides were known to react with dilute base to form insoluble dialkyltin oxides, possibly via short-lived dihydroxide intermediates (3). This reaction could also occur in water but the rate was not well defined. Meinema, in determining the solubility of dibutyltin dichloride in seawater, prepared a 20-ppm solution and observed precipitation after stirring two hours. After four days, 6-8 ppm dibutyltin species remained in solution (1).

Dissociation or reaction (or both) accounted for the poor extractability of dibutyltin dichloride into organic solvents, and for the good extractability in the presence of acid, as both processes are reversible. In our studies, aqueous solutions were prepared just prior to extraction to minimize oxide formation. No precipitate was ever observed in 1-2 ppm Sn aqueous solutions of dibutyltin dichloride.

The fourth possibility was that reaction to the bromide form occurred in the hot injection port of the gas chromatograph and was an experimental artifact. This explanation suffered the same drawback as the first in that it did not explain why the hydrobromic acid was necessary for good extraction efficiency. The amount of hydrobromic acid in the concentrated benzene extract was not measured, but was thought to be significant. Back-extracting the benzene extract with water to remove hydrobromic acid in order to protect our instruments from high acid concentrations resulted in >50% loss of tin back into the aqueous phase. Drying the organic extract with sodium sulfate also caused considerable (20-35%) loss of organotin.

Dibutyltin-bis-laurylmercaptide Extraction--

Dibutyltin-bis-laurylmercaptide is a compound representative of one class of commercial stabilizers. An aqueous dibutyltin-bis-laurylmercaptide solution, containing 2 ppm Sn, was prepared from an acetone stock solution containing 1000 ppm Sn. After acidification with hydrobromic acid to 2% (v/v) acid, it was immediately extracted with benzene. An aliquot of the non-acidified stock solution and the concentrated extract were individually chromatographed on a 3% (w/w) OV-17 column, held at 100°C for two minutes, then temperature programmed to 240°C at 8°/minute. The column was primed with two injections of dibutyltin dichloride stock solution prior to use to enhance the appearance of organotin compounds. The chromatogram of the acetone stock solution revealed a few low-level impurity peaks but the dibutyltin-bis-laurylmercaptide did not chromatograph.

The chromatogram of the concentrated benzene extract of this aqueous acidified solution of dibutyltin-bis-laurylmercaptide (Figure A-2) contained a major degradation product peak with a retention time of 10.3 minutes. The mass spectrum of this degradation product (Figure A-3) matched the mass spectrum of lauryl mercaptan in benzene. This was not surprising since the tin-sulfur bond is quite reactive in acid. The lack of evidence of dibutyltin dihalide in these mass spectra indicated that either its concentration was below the detection limit (100 ng) or a non-chromatographable dibutyltin mercaptide halide formed after only one lauryl mercaptan chain was removed from each molecule.

Dibutyltin-bis-isooctylthioglycolate Extraction--

Dibutyltin-bis-isooctylthioglycolate and its dimethyltin analog represent the major class of CPVC/PVC stabilizers. An aqueous dibutyltin-bis-isooctylthioglycolate solution, containing 2 ppm Sn, was prepared from an acetone stock solution and extracted with benzene after acidification with hydrobromic acid. An aliquot of the stock solution and the concentrated extract were individually chromatographed on a 3% (w/w) OV-17 column, held at 80°C for 4 minutes, then temperature programmed to 240°C at 16°/minute. The chromatogram of the acetone stock solution (Figure A-4) revealed a series of impurities or degradation products concentrated in two broad peaks with retention times of ∿6 and ∿14 minutes. The chromatogram of the concentrated benzene extract (Figure A-5) yielded a strong, two-component degradation product peak with a retention time corresponding to the valley between the two peaks observed in the chromatogram of the acetone stock solution. The mass spectrum of each component of the degradation product peak showed the presence of an octyl group, but molecular ions were not present. An acetone solution of the reference material, isooctyl thioglycolate, produced two peaks when chromatographed, as seen in Figure A-6. The retention times and mass spectra of the two components of the extract sample peak matched those of the reference compound, except that the extract sample mass spectra showed peaks at 150 and 152 atomic mass units, neither of which appeared in the isooctyl thioglycolate spectrum. These ions were very weak in the sample spectrum and could represent third-component impurities or differences in quantity of sample scanned. There was evidence of dibutyltin dibromide (at masses 335 and 337) in two scans, but it accounted for only a small portion of the ∿14-minute peak in which it occurred.

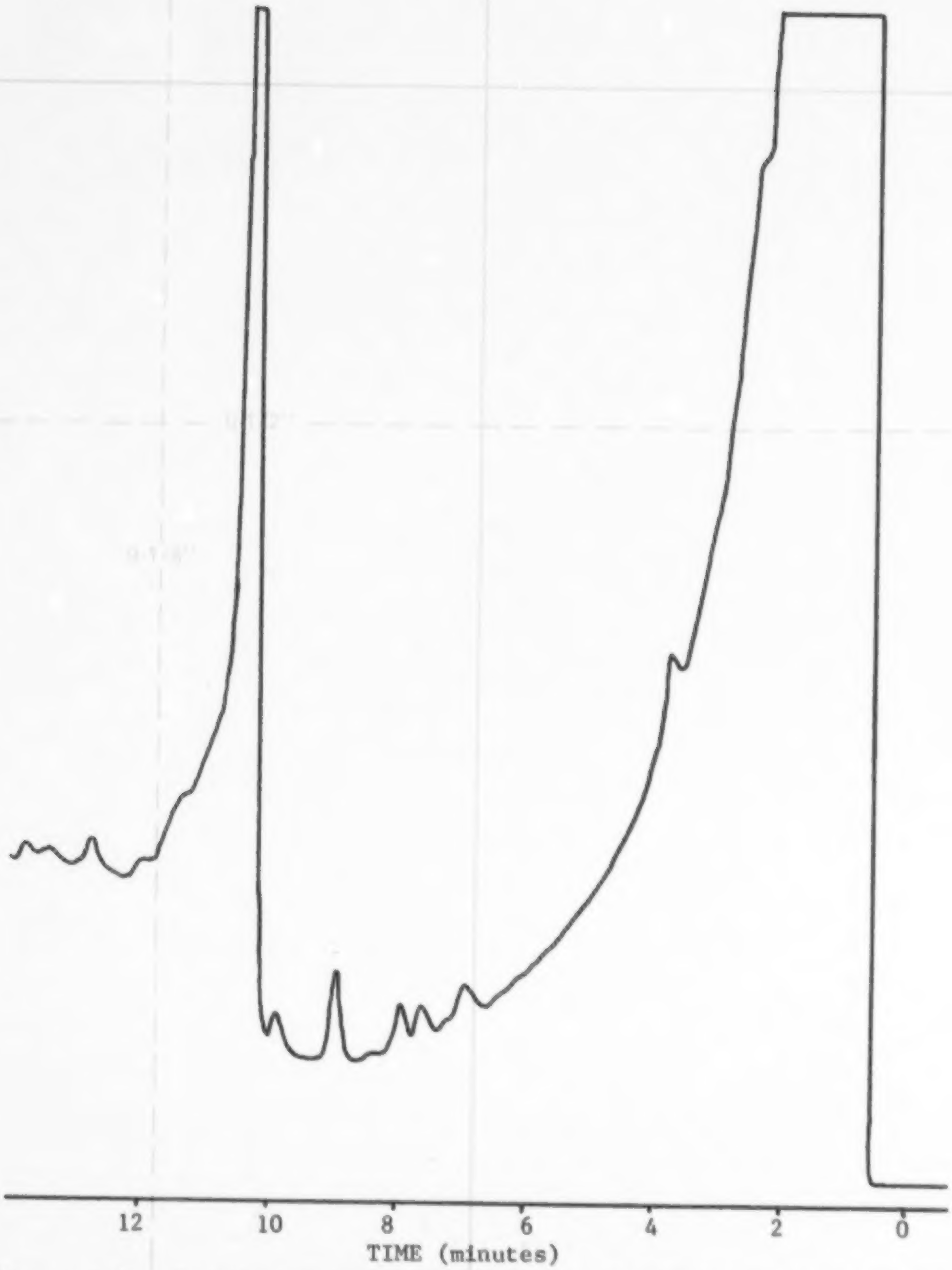

Figure A-2. Gas chromatogram of a concentrated hydrobromic acid/benzene extract of a dibutyltin-bis-laurylmercaptide water solution.

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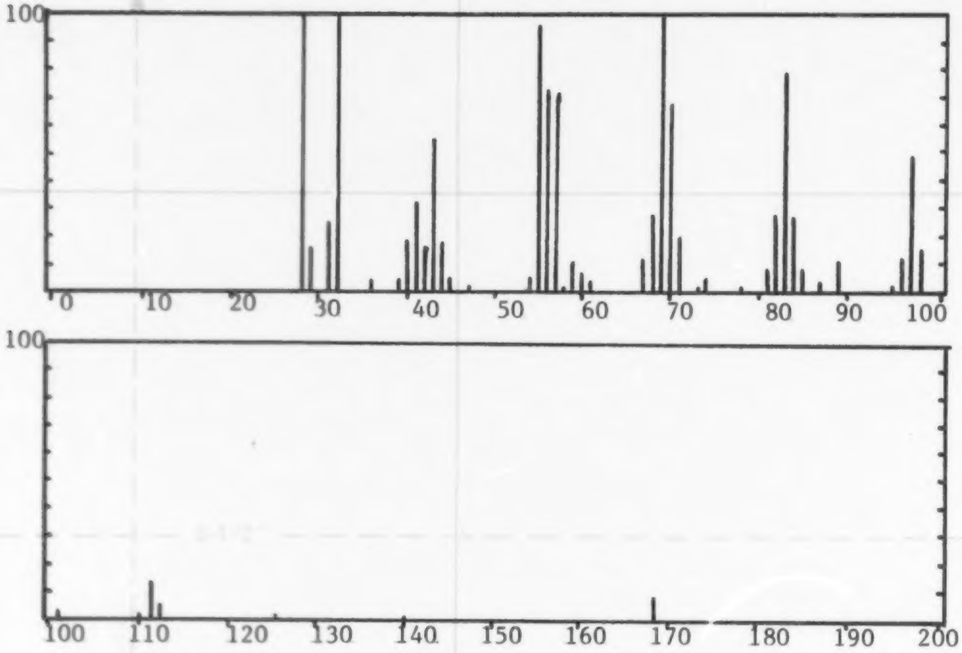

Figure A-3. Mass spectrum of dibutyltin-bis-laurylmercaptide extraction degradation product.

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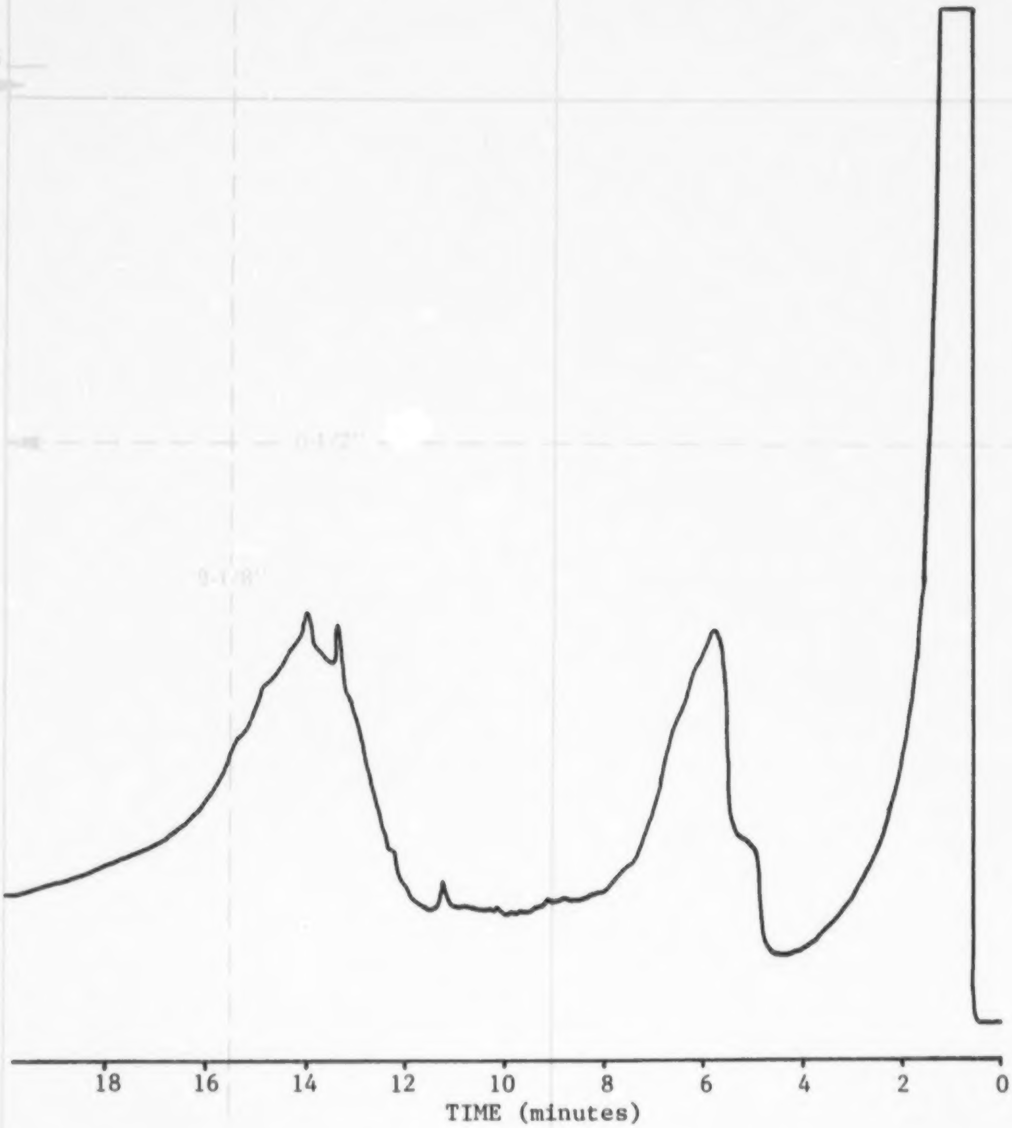

Figure A-4. Gas chromatogram of dibutyltin-bis-isooctylthioglycolate acetone stock solution.

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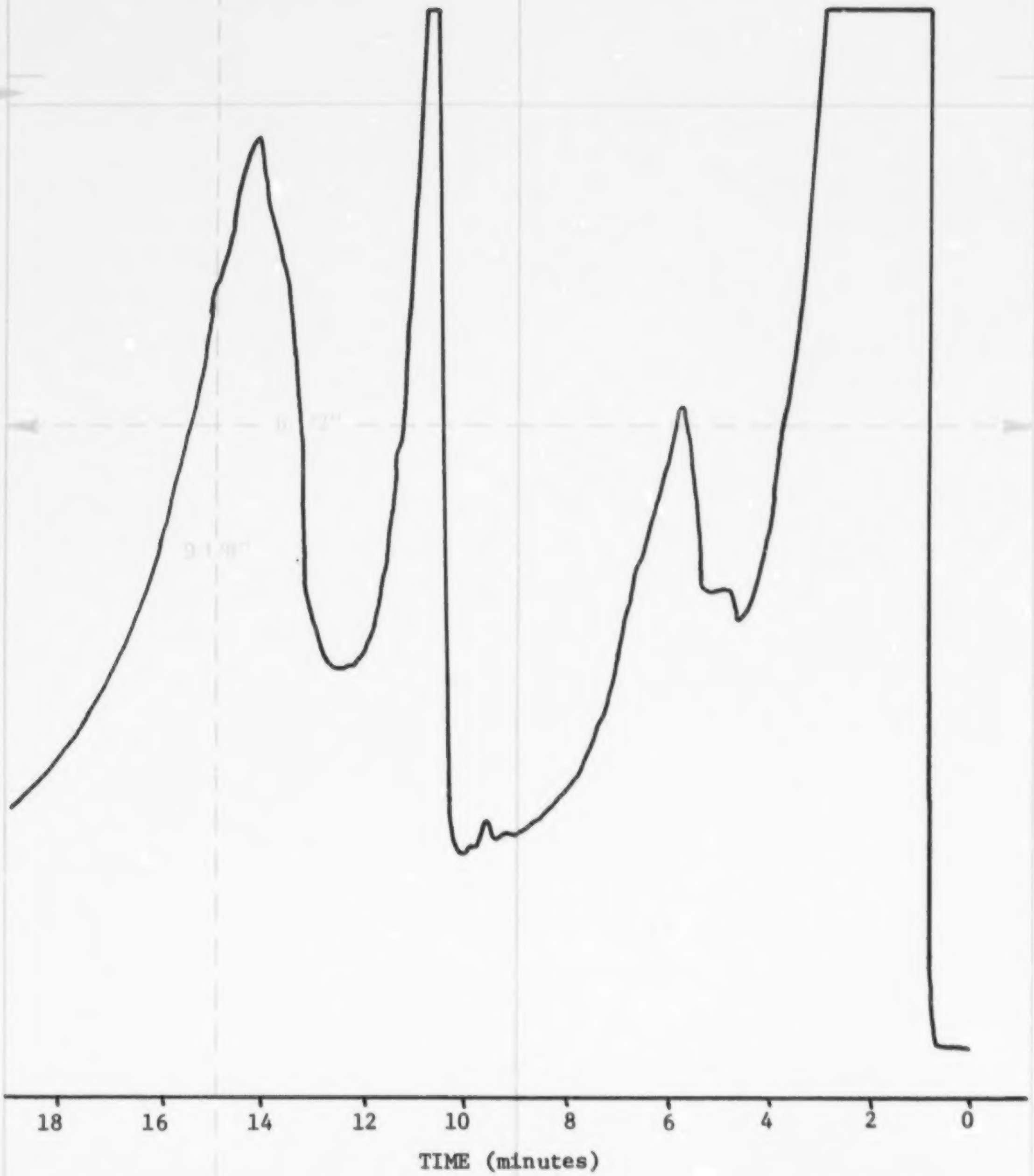

Figure A-5. Gas chromatogram of a concentrated hydrobromic acid/benzene extract of a dibutyltin-bis-isooctylthioglycolate water solution.

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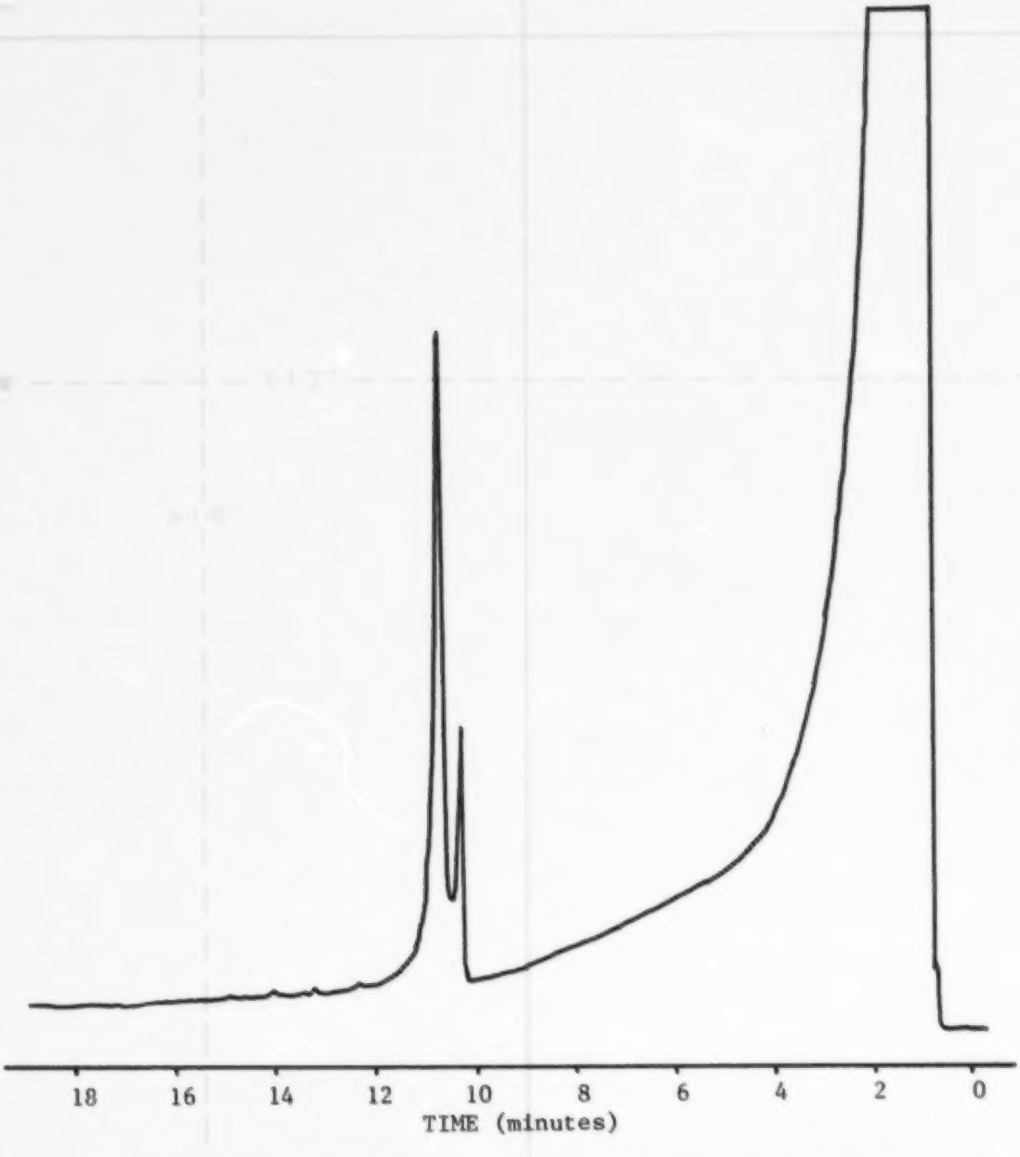

Figure A-6. Gas chromatogram of isooctyl thioglycolate.

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Two commercial stabilizers, G (a methyltin mercaptide suspected to be isooctylthioglycolate) and H (known to be dibutyltin-bis-isooctylthioglycolate) were also tested. The acetone stock solutions of each of these stabilizers produced a number of chromatographic peaks including two having the same retention times and mass spectra as the two dibutyltin-bis-isooctylthioglycolate extract degradation products discussed previously.

Flameless Atomic Absorption

The applicability of flameless atomic absorption to the analysis of total tin was investigated. Optimization for tin was accomplished by determining the proper times and temperatures for the DRY, ASH, and ATOMIZE cycles. The times varied with the matrix of the samples being routinely analyzed. In the initial investigations with aqueous samples times of 15, 30, and 10 seconds seemed satisfactory for the DRY, ASH, and ATOMIZE cycles, respectively. The temperature settings for the cycles were more critical, however. Using the experience of others as a guide, the temperature for the DRY cycle was set at 110°C (6 amps) and that for the ASH cycle at 700°C (40 amps). Further work showed that an 800°C (45 amps) ASH temperature was a better choice. ATOMIZE cycle temperatures were examined over a range from 2000°C to 2550°C (150-250 amps). For a given sample the response in terms of absorbance was found to increase with increasing temperature. At 2400°C (220 amps) and above, memory effects were not observed, and the need for post-analysis rod cleanup was eliminated. Thereafter an ATOMIZE temperature of 2550°C (250 amps) was used for ppb-level investigations. For work at the ppm level, a 2000°C temperature appeared adequate and less destructive to the graphite rods, but rod cleanup was necessary after sample analysis.

It was established by using a 1-ppm standard and making injections in the range of 0.5 to 1.0 µL, that 0.5 ng Sn was within the working range of the graphite rod furnace, inasmuch as 0.02 ppm Sn could theoretically be detected after such sample injections. At the one-nanogram level, the relative standard deviations of successive observations of standards varied from 2 to 5%, while the range at the half-nanogram level was 5 to 11%.

During the course of the XAD-2 resin and liquid-liquid extraction studies, standards of dibutyltin dichloride were prepared in a variety of solvents and analyzed by flameless atomic absorption. Substantial matrix effects were noted. Aqueous standards of dibutyltin dichloride gave flameless atomic absorption responses equal to the responses of acidified aqueous standards of inorganic tin. The inclusion of acid in the aqueous dibutyltin dichloride standard, or preparation of the standard in an organic solvent led to a lower flameless atomic absorption response. Results are listed in Table A-2. Three of the halogenated solvents gave the lowest responses; carbon tetrachloride gave essentially no response, and trichloroethylene and tetrachloroethylene gave small responses which seemed to be independent of tin concentration.

High-Pressure Liquid Chromatography (HPLC)

The ultraviolet absorption spectra of dibutyltin dichloride, dibutyltin-bis-isooctylthioglycolate, dibutyltin-bis-laurylmercaptide, and a number of

TABLE A-2. RELATIVE FLAMELESS ATOMIC ABSORPTION RESPONSES OF 1 PPM SN STANDARDS IN VARIOUS MATRICES

Sn Source and Matrix	Relative Response
Inorganic Sn in water, 1.4% Hydrochloric acid	1
Dibutyltin dichloride in water	1
Dibutyltin dichloride in water, 0.5% Hydrobromic acid	0.8
Dibutyltin dichloride in water, 2.0% Hydrobromic acid	0.5
Dibutyltin dichloride in benzene	0.8
Dibutyltin dichloride in acetone	0.7
Dibutyltin dichloride in hexane	0.4
Dibutyltin dichloride in methanol	0.8
Dibutyltin dichloride in diethyl ether	0.6
Dibutyltin dichloride in methylene chloride	0.4
Dibutyltin dichloride in 1,1,1-trichloroethane	0.5
Dibutyltin dichloride in carbon tetrachloride	<0.1
Dibutyltin dichloride in trichloroethylene	∿0.1
Dibutyltin dichloride in tetrachloroethylene	∿0.1
Dibutyltin-bis-laurylmercaptide in water	0.8
Dibutyltin-bis-isooctylthioglycolate in water	1.0

commercial stabilizers were obtained in hexane using a recording spectrophotometer. Each of the stabilizer compounds showed major absorption at 210 nm, with minor absorption bands at 230-260 nm. For some compounds there was a considerable (up to 15 nm) shift in the wavelength of the absorption maximum at higher concentrations. The 210-nm absorptivities of these compounds ranged from 1.3 to 1.7 mm^{-1} $(mg/mL)^{-1}$.

On the basis of these absorptivities and the path length and sensitivity of our Spectro Monitor III variable-wavelength ultraviolet absorption detector for HPLC, the theoretical detection limits for these stabilizer compounds at 210 nm were less than 2 ng each. Achievement of these theoretical limits was unlikely since many solvents used in the HPLC mobile phase also absorbed at 210 nm, making maximum sensitivity unobtainable.

Using an EM Laboratories LiChrosorb Si 60 5μ normal-phase column or a Whatman Partisil PXS 5/25 ODS reverse-phase column with a variety of mobile phases, the only compound affording satisfactory results was dibutyltin dihydride. Dibutyltin dichloride gave very erratic results while dibutyltin-bis-isooctylthioglycolate and dibutyltin-bis-laurylmercaptide were not eluted from either column. Although others (4) have separated alkyltin halides by HPLC, we found this technique to be of limited usefulness. Ion-pair and high-pressure ion-exchange chromatography may be more suitable for organotin compounds.

Thin-Layer Chromatography (TLC)

TLC was investigated as a method for isolating intact stabilizer from aqueous extracts. Benzene solutions (∿2.5μg/μL) of dibutyltin-bis-isooctylthioglycolate and dibutyltin dichloride were prepared and 5-30 μL of each spotted on glass plates coated with Silica Gel G. Using a solvent system of 40:4:1 hexane/acetone/acetic acid, the Rf values of these two compounds were determined after spraying the dried plates with 0.1% (w/v) dithizone in chloroform. The identical Rf values indicated that both migrated at the same rate or, more likely, were converted to the same dibutyltin species, i.e. Bu_2Sn^{++}, which migrated. The TLC methods, described in the literature use 0.1 - 5% (v/v) acetic acid in the solvent system. Since dibutyltin dichloride ionizes in acetone, acids, and alcohols, it was reasonable to expect that the migrating species were ionic.

Triplicate analyses of the aforementioned compounds plus dibutyltin-bis-laurylmercaptide and dibutyltin oxide polymer were performed using the hexane/acetone/acetic acid solvent (40:4:1). All the compounds except the oxide yielded similar and reproducible Rf values (0.24 - 0.26). This verified the similarity of the nature of the migrating species, i.e. Bu_2Sn^{++}. These observations agree with the findings of Burger (5), who concluded that the Rf values of the organotin compounds he investigated were actually those of the cationic portion of the molecule. The Bu_2Sn^{++} spot on a Silica Gel G plate was colored red or orange/red after spraying with 0.1% (w/v) dithizone in chloroform. The sulfur-containing organotin compounds, while having the same Rf value as dibutyltin dichloride, were distinguishable by the presence of an additional blue spot for the sulfur-containing moiety. This blue spot for isooctylthioglycolate had an Rf value of 0.5 while that of lauryl mercaptan had an Rf value of 0.74. The two stabilizers could be differentiated using the TLC system described above.

Gas Chromatography

Gas chromatography with flame ionization detection was evaluated for its applicability in separating alkyltin halides. It was found that dibutyltin dichloride could be chromatographed on 3% (w/w) OV-17, 3% (w/w) SE-30, and 10% (w/w) SP-1000 columns if the column had been conditioned with injections of dibutyltin dichloride prior to analysis. The detection limit, about two micrograms, was poor. Tributyltin chloride also chromatographed reasonably well, but butyltin trichloride produced only a small, very broad peak. Some improvement in sensitivity could undoubtedly have been gained by using electron capture or microcoulometric detection. The basic problem seemed to be that a certain portion of the injected sample was retained on the column. Since the priming effect diminished with time, good quantitative results were very difficult to obtain. Methyltin chlorides did not chromatograph.

A 1μL/mL standard of dibutyltin dihydride in diethyl ether was prepared and a portion analyzed by gas chromatography on a 3% (w/w) OV-17 column with flame ionization detection. A sharp peak was observed. By extrapolation, the detection limit should be 0.1 - 0.01 μg/injection. This detection limit was considerably better than that for dibutyltin dichloride. Tributyltin hydride chromatographed equally well, but butyltin trihydride and the methyltin hydrides did not chromatograph. Most of the alkyltin hydrides were air sensitive and required handling in closed systems to obtain good quantitative results.

Tetraalkyltin compounds chromatographed very well and had flame ionization detection limits in the nanogram range. The magnitudes of the detection limits depended on the alkyl chains. Methyl- and ethyltin compounds were quite volatile and had to be chromatographed on a Porapak P or other porous polymer column. Butyltin and methylbutyltin compounds chromatographed well on a 3% (w/w) OV-17 column, temperature programmed at 16°/minute from 80 to 200°C. Butyltrimethyl tin had a retention time close to that of the solvent peak, thus limiting the sensitivity.

The stabilizers did not chromatograph on conventional columns. Since there was some concern that some portion of the stabilizer used in PVC and CPVC pipe could be extracted in its original form, we searched briefly for a stationary phase applicable to these compounds. A 3-foot, 2-mm internal diameter column packed with 0.1% (w/w) OV-17 on 80/100 mesh glass beads was available. An attempt was made to chromatograph dibutyltin-bis-isooctylthioglycolate and dibutyltin-bis-laurylmercaptide on this column. The isooctylthioglycolate gave no peak, but the laurylmercaptide gave one or two peaks depending on temperature.

Mass Spectrometry

Mass spectrometry was used, alone or in combination with gas chromatography, to provide positive identification of organotin compounds. Mass spec-

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tra of a number of organotin and related compounds were prepared for use both as reference spectra on our instrument and in choosing masses for ion monitoring.

Figures A-7 through A-15 show the mass spectra of a variety of organotin compounds. The organotin compounds generally showed very characteristic ions at the molecular weight minus one alkyl chain, but no molecular ions. Alkyltin chlorides generally showed some alkyltin bromide contamination. Mass spectra of the two stabilizer compounds are not presented here, but dibutyltin-bis-laurylmercaptide yielded very strong peaks at masses corresponding to a loss of one lauryl mercaptan chain. Lauryl mercaptan masses 201 and 202 were the only other strong peaks in the spectrum. Dibutyltin-bis-isooctylthioglycolate had more fragmentation, as a result of successive losses of both butyl and octyl groups.

Calculated versus observed isotope abundances are included on most spectra. Tin has a total of ten isotopes (only the 3-5 major isotopes were used in the calculated abundances). Maintaining an awareness of the envelope of isotope peaks aided in determining the quality of the spectrum, particularly when a sharp chromatographic peak with a rapidly changing sample concentration was scanned.

EPA Form 2350-4 (4-80)
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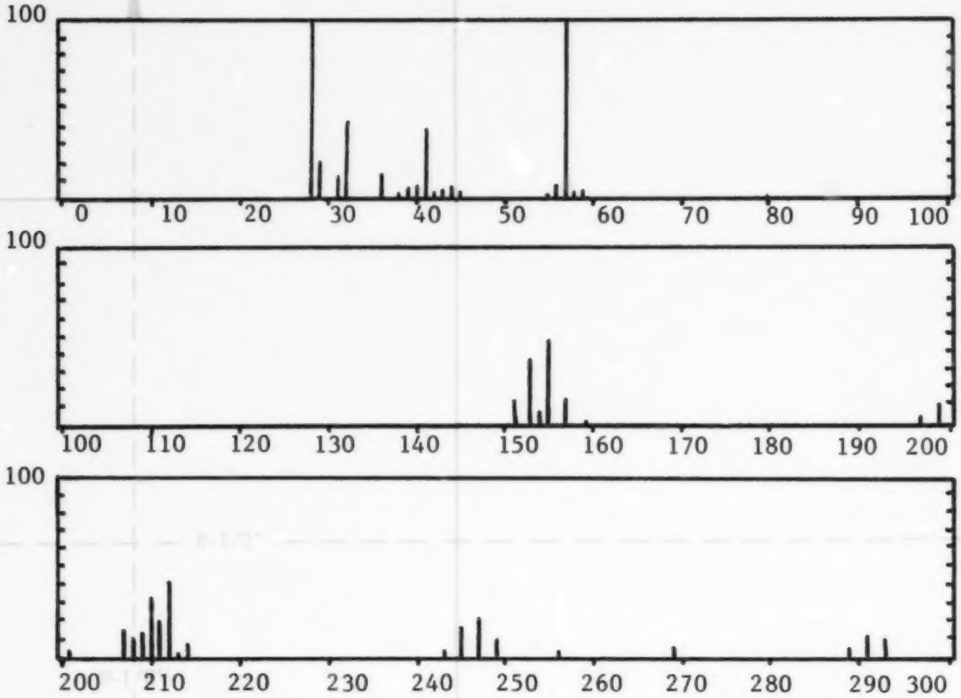

Figure A-7. Mass spectrum of dibutyltin dichloride.

Explanation: Calculated versus observed isotope abundances are included to aid in determining the quality of the spectrum.

		Relative Abundance	
Mass	Assignment	Calculated	Observed
243	*$Bu^{116}Sn^{35}Cl_2$	0.19	0.15
245	$Bu^{118}Sn^{35}Cl_2$, $Bu^{116}Sn^{35}Cl^{37}Cl$	0.66	0.75
247	$Bu^{120}Sn^{35}Cl_2$, $Bu^{118}Sn^{35}Cl^{37}Cl$, $Bu^{116}Sn^{37}Cl_2$	1.0	1.0
249	$Bu^{120}Sn^{35}Cl^{37}Cl$, $Bu^{118}Sn^{37}Cl_2$	0.56	0.50
251	$Bu^{120}Sn^{37}Cl_2$	0.16	-

*Bu is n-butyl.

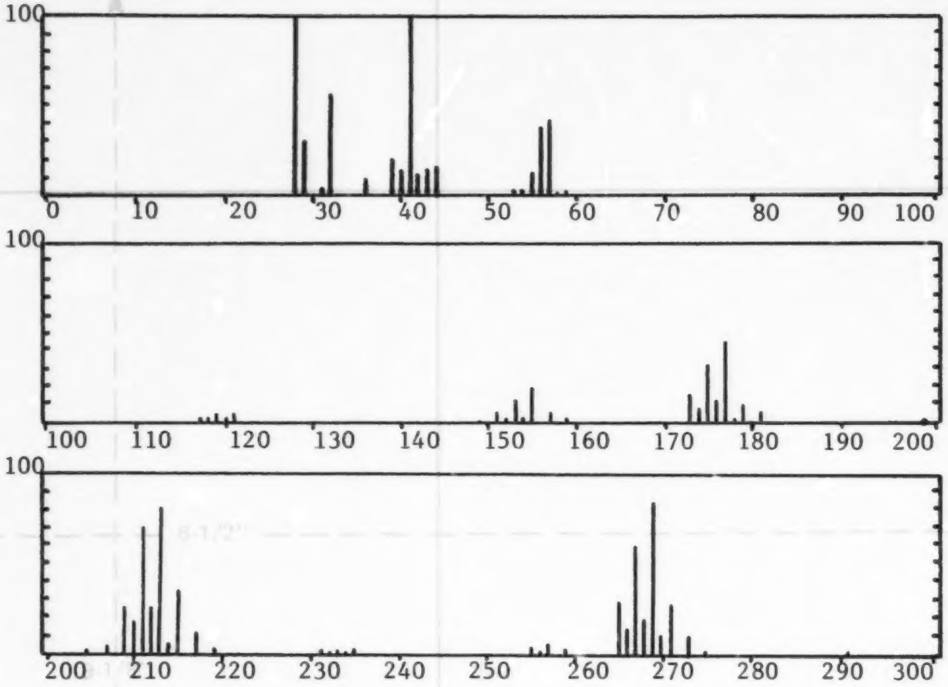

Figure A-8. Mass spectrum of tributyltin chloride.

Explanation: Calculated versus observed isotope abundances are included to aid in determining the quality of the spectrum.

Mass	Assignment	Relative Abundance Calculated	Relative Abundance Observed
265	$^*Bu_2{}^{116}Sn^{35}Cl$	0.35	0.35
267	$Bu_2{}^{116}Sn^{37}Cl$, $Bu_2{}^{118}Sn^{35}Cl$	0.71	0.72
269	$Bu_2{}^{118}Sn^{37}Cl$, $Bu_2{}^{120}Sn^{35}Cl$	1.0	1.0
271	$Bu_2{}^{120}Sn^{37}Cl$	0.26	0.35
273	$Bu_2{}^{122}Sn^{35}Cl$	0.12	0.15

*Bu is n-butyl.

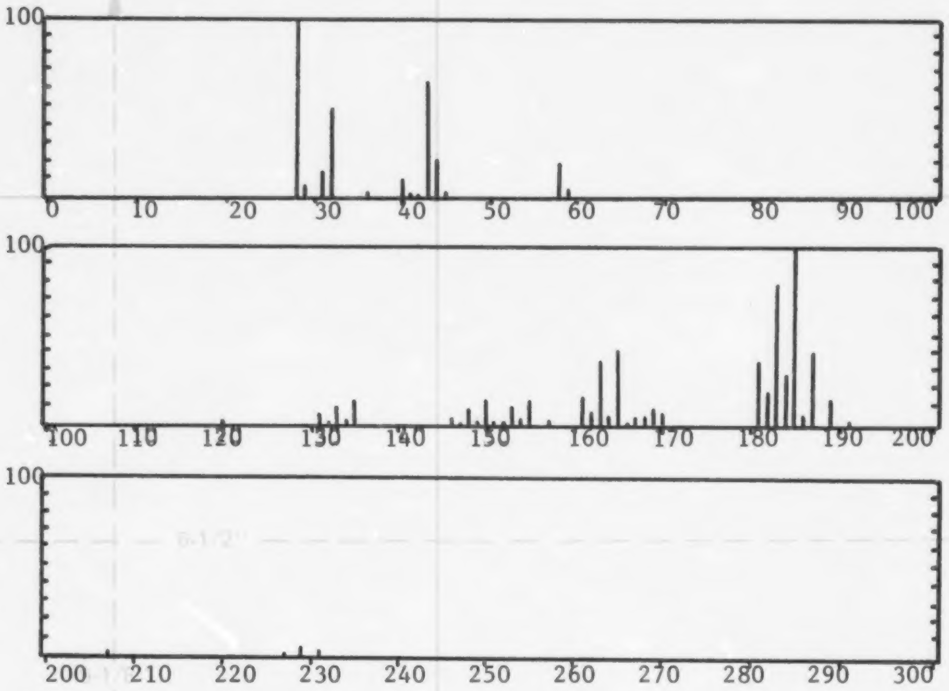

Figure A-9. Mass spectrum of trimethyltin chloride.

Explanation: Calculated versus observed isotope abundances are included to aid in determining the quality of the spectrum.

		Relative Abundance	
Mass	Assignment	Calculated	Observed
181	*$Me_2\,^{116}Sn\,^{35}Cl$	0.35	0.35
183	$Me_2\,^{116}Sn\,^{37}Cl$, $Me_2\,^{118}Sn\,^{35}Cl$	0.71	0.78
185	$Me_2\,^{118}Sn\,^{37}Cl$, $Me_2\,^{120}Sn\,^{35}Cl$	1.0	1.0
187	$Me_2\,^{120}Sn\,^{37}Cl$	0.26	0.41
189	$Me_2\,^{122}Sn\,^{35}Cl$	0.12	0.15

*Me is methyl.

EPA-287 (Cin.)
(4-75)

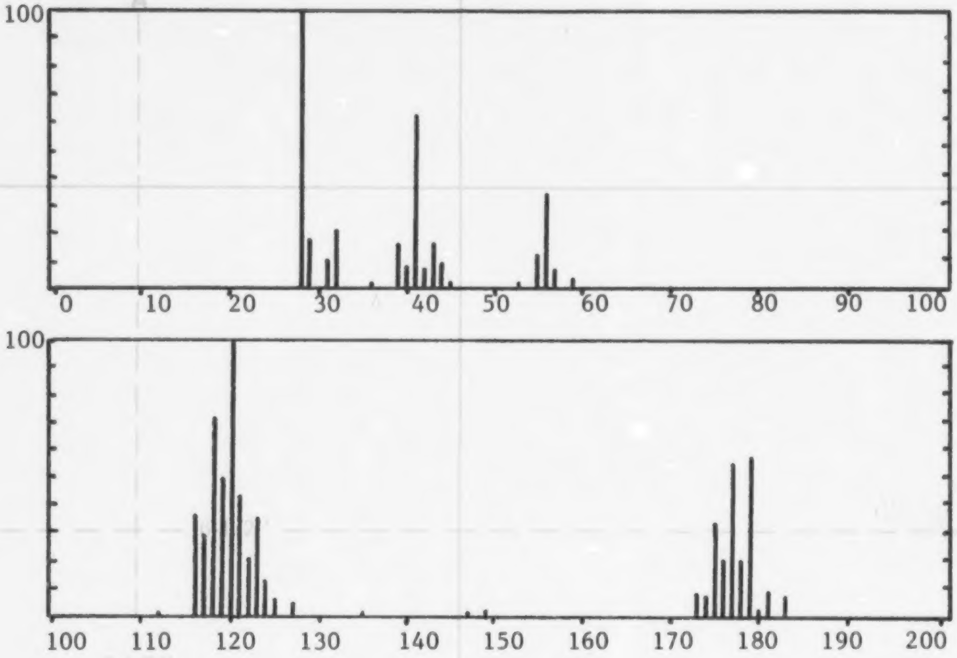

Figure A-10. Mass spectrum of dibutyltin dihydride.

Explanation: Calculated versus observed isotope abundances are included to aid in determining the quality of the spectrum.

		Relative Abundance	
Mass	Assignment	Calculated	Observed
116	^{116}Sn	0.44	0.37
118	^{118}Sn	0.73	0.72
120	^{120}Sn	1.0	1.0
122	^{122}Sn	0.14	0.21
124	^{124}Sn	0.18	0.13

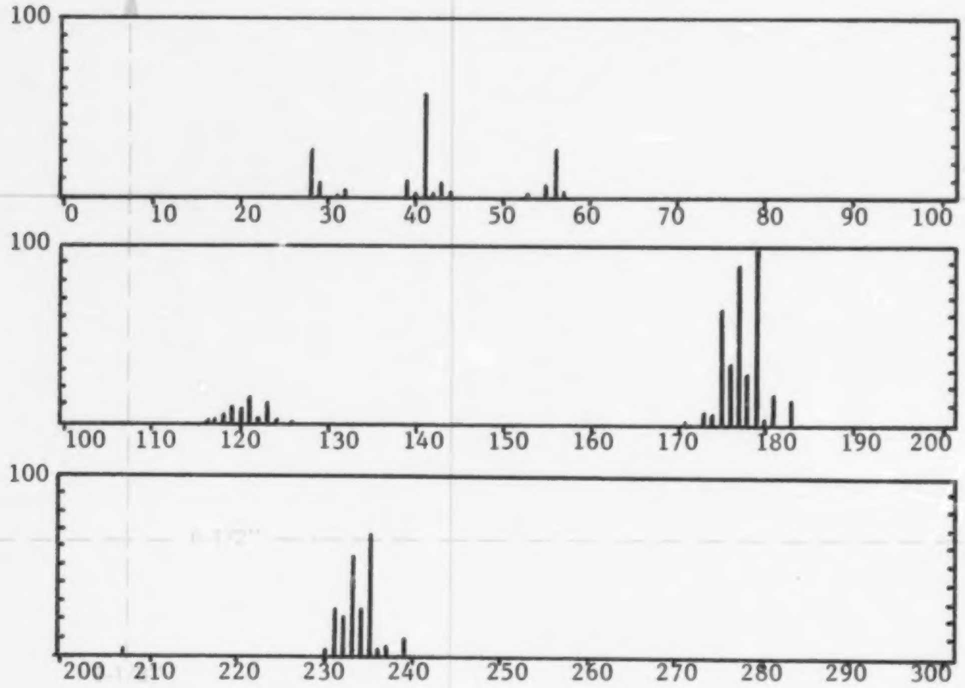

Figure A-11. Mass spectrum of tributyltin hydride.

Explanation: Calculated versus observed isotope abundances are included to aid in determining the quality of the spectrum.

Mass	Assignment	Relative Abundance	
		Calculated	Observed
231	$Bu_2{}^{116}SnH$	0.44	0.37
233	$Bu_2{}^{118}SnH$	0.73	0.83
235	$Bu_2{}^{120}SnH$	1.0	1.0
237	$Bu_2{}^{122}SnH$	0.14	0.07
239	$Bu_2{}^{124}SnH$	0.18	0.14

EPA-287 (Cin.)
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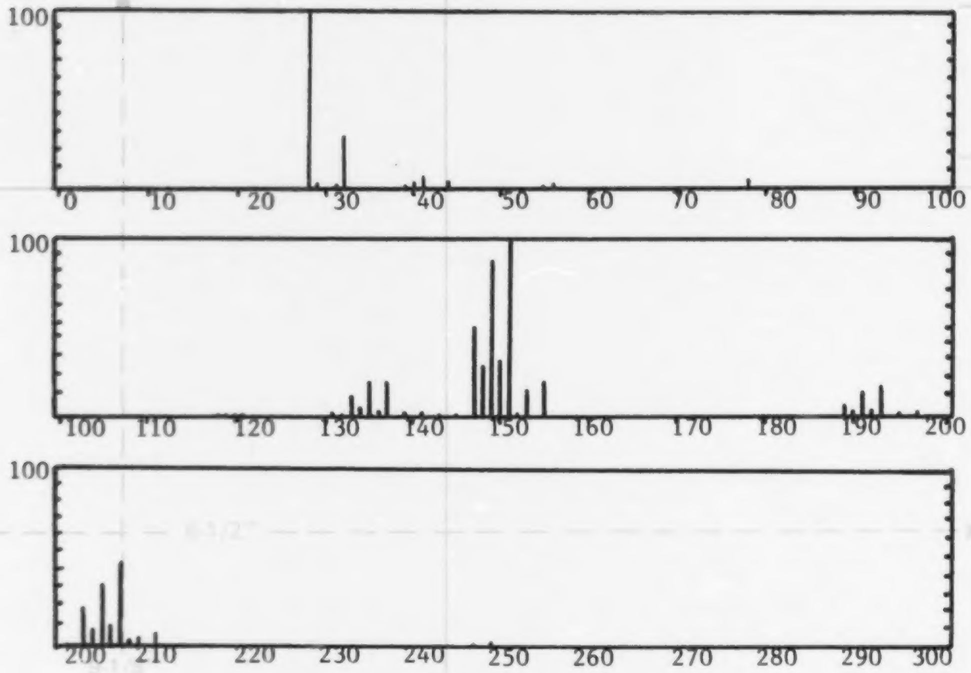

Figure A-12. Mass spectrum of dibutyldimethyl tin.

Explanation: Calculated versus observed isotope abundances are included to aid in determining the quality of the spectrum.

Mass	Assignment	Relative Abundance Calculated	Relative Abundance Observed
203	$^*BuMe_2{}^{116}Sn$	0.44	0.45
205	$BuMe_2{}^{118}Sn$	0.73	0.75
207	$BuMe_2{}^{120}Sn$	1.0	1.0
209	$BuMe_2{}^{122}Sn$	0.14	0.10
211	$BuMe_2{}^{124}Sn$	0.18	0.16

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*Bu is n-butyl and Me is methyl.

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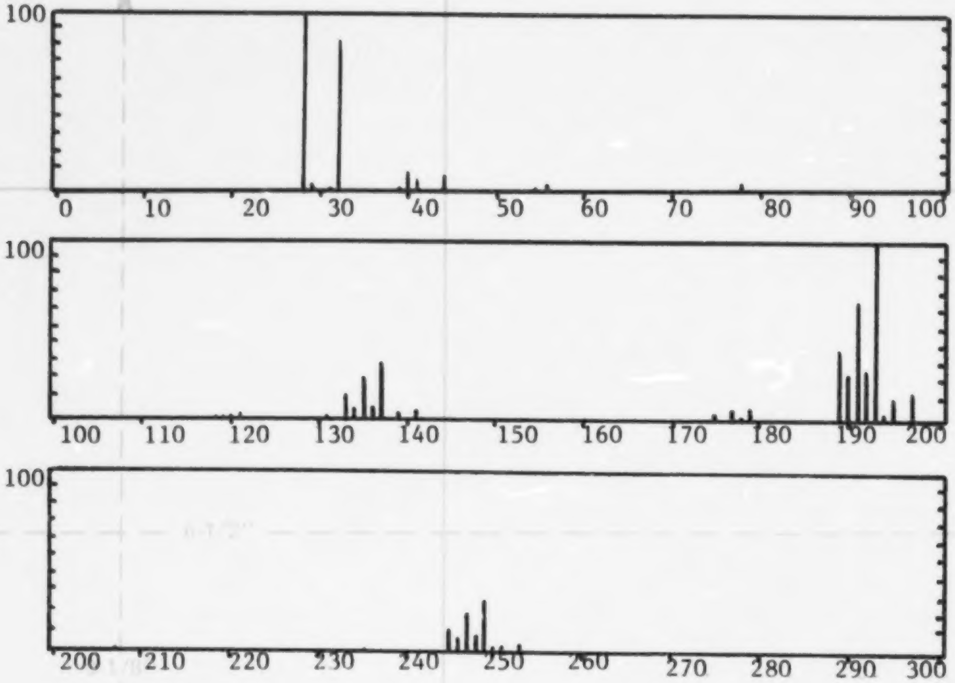

Figure A-13. Mass spectrum of tributylmethyl tin.

Explanation: Calculated versus observed isotope abundances are included to aid in determining the quality of the spectrum.

Mass	Assignment	Relative Abundance Calculated	Relative Abundance Observed
245	*$Bu_2Me^{116}Sn$	0.44	0.42
247	$Bu_2Me^{118}Sn$	0.73	0.76
249	$Bu_2Me^{120}Sn$	1.0	1.0
251	$Bu_2Me^{122}Sn$	0.14	0.09
253	$Bu_2Me^{124}Sn$	0.18	0.13

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* Bu is n-butyl and Me is methyl.

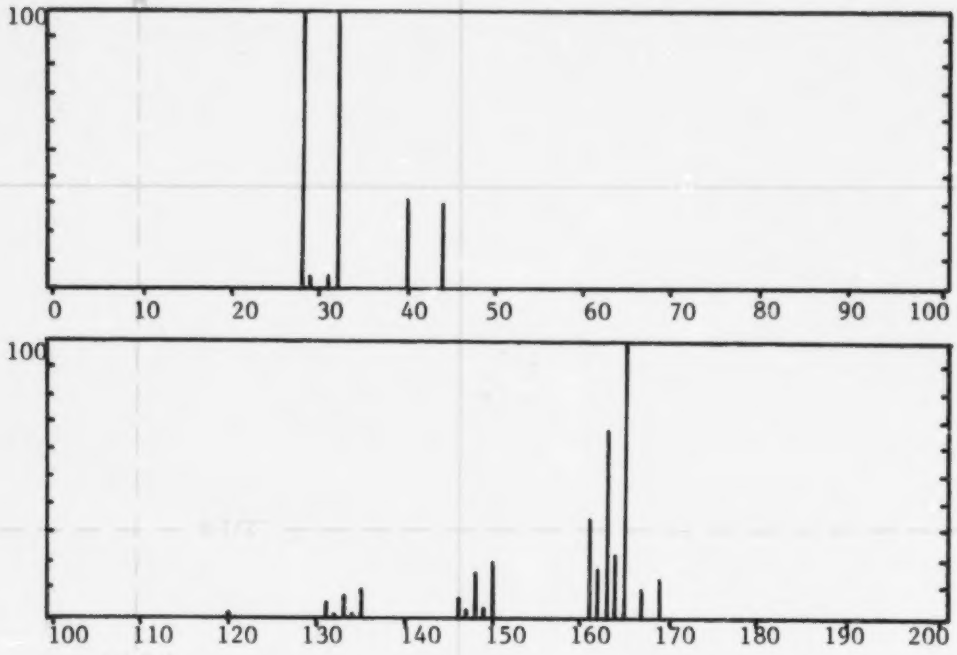

Figure A-14. Mass spectrum of tetramethyl tin.

Explanation: Calculated versus observed isotope abundances are included to aid in determining the quality of the spectrum.

Mass	Assignment	Relative Abundance Calculated	 Observed
161	$Me_3{}^{116}Sn$	0.44	0.37
163	$Me_3{}^{118}Sn$	0.73	0.69
165	$Me_3{}^{120}Sn$	1.0	1.0
167	$Me_3{}^{122}Sn$	0.14	0.11
169	$Me_3{}^{124}Sn$	0.18	0.15

EPA-287 (Cin.)
(4-76)

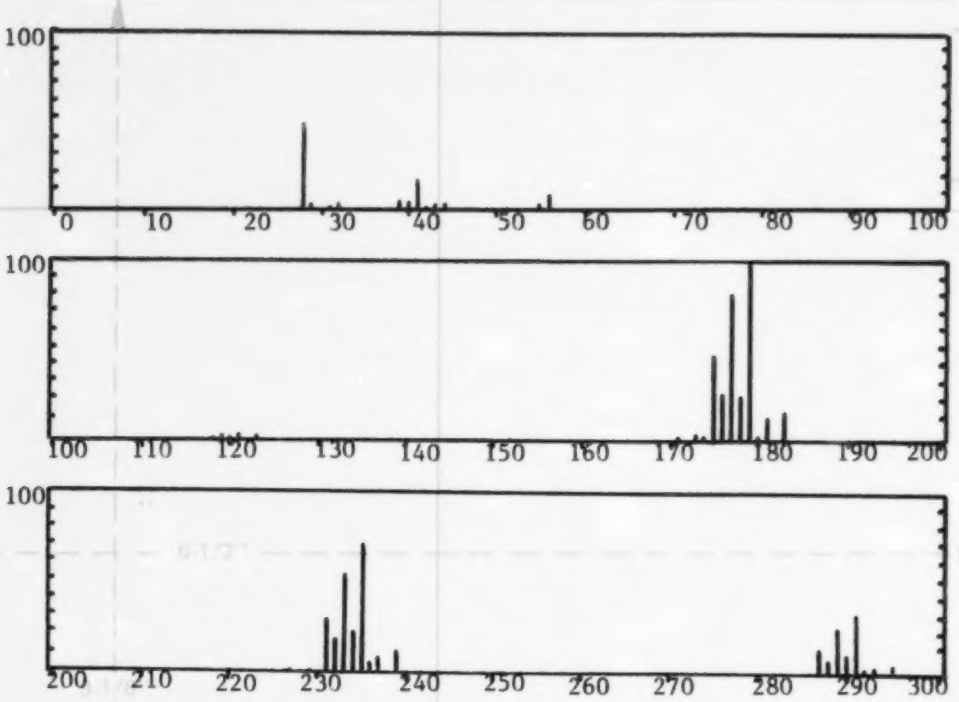

Figure A-15. Mass spectrum of tetrabutyl tin.

Explanation: Calculated versus observed isotope abundances are included to aid in determining the quality of the spectrum.

Mass	Assignment	Relative Abundance Calculated	Relative Abundance Observed
287	$Bu_3{}^{116}Sn$	0.44	0.42
289	$Bu_3{}^{118}Sn$	0.73	0.76
291	$Bu_3{}^{120}Sn$	1.0	1.0
293	$Bu_3{}^{122}Sn$	0.14	0.12
295	$Bu_3{}^{124}Sn$	0.18	0.14

EPA-287 (Cin.)
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APPENDIX REFERENCES

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